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Surfactants and Desensitizing Wax Substitutes for TNT-Based Systems

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Air Force Materiel Command ■ United States Air Force ■ Eglin Air Force Base

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FOR THE COMMANDER

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Technical Director, Munitions Division

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MACH I, Inc. developed three polyvinylpyrrolidones (Ganex resins) that are effective emulsifiers for microcrystalline or selected substitute desensitizing waxes in AFX-644 TNT melt cast bomb explosive. Ganex resins also are excellent dispersants for TNT melt casting and PBX in which they provide important benefits: wetting, coating, dispersion, lubrication, thinning, void filling, desensitization, and increased production rate.

Ganex resins are expected to be effective emulsifiers and dispersants with microcrystalline desensitizing waxes or the recommended substitutes in any melt cast system such as Compositions B, HBX-1, D-2, and H-6.

Furthermore, by reducing viscosity Ganex resins are expected to facilitate processing of PBX compositions such as AFX-931 in batch mixers as well as continuous mixers (e.g., twin-screw extruders). The Ganex surfactants appear promising for use in most munitions mixing processes for production of: ammunition, bombs, missiles, projectiles, demolition charges and special purpose devices.

MACH I, Inc. also developed promising polar wax substitutes, having different desensitizing mechanisms, to enhance the benefits cited above. These substitutes offer greater formulation flexibility than conventional waxes to mitigate possible fuzing insensitivity or loss of explosive power. In contrast to conventional desensitizing wax, they are easier to emulsify and are dependably available in ample quantity and consistent quality.

14. SUBJECT TERMS
Explosive
Pyrotechnic
TNT
Melt Casting
Emulsifier
Desensitizer
Wax
Oil
Wax Substitute
PBX Compounding
Dispersant

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EXECUTIVE SUMMARY

Microcrystalline wax presently used to desensitize cast explosives suffers from:

- Undependable physical/chemical properties
- Unpredictable cost
- Uncertain supply
- Formulation constraints

Established desensitizing formulations (such as Composition D-2) that contain wax, nitrocellulose and lecithin emulsifier cause these problems:

- Varying viscosity, hence processing difficulty
- Defects in the casting
- Fouling of processing equipment
- Gassing of the cast explosive
- Classification as an explosive, thus complicating storage and handling.

Under Contract F08630-92-C-0058 MACH I, Inc. has conducted for WL/MNME a two-year, Phase II SBIR program to develop advanced desensitizing systems based on microcrystalline and superior synthetic waxes. The program comprised six tasks:

1. Review literature
    A. Wax technology and economics
    B. Selection criteria for military applications
2. Identify process and methodology for selection of explosive matrix/wax/emulsifier system.
3. Identify candidate waxes/surfactants for a given explosive matrix.
    A. Various waxes
    B. Various wax substitutes
    C. Various surfactants
4. Evaluate candidate systems for
    A. Miscibility
    B. Stability
    C. Compatibility
   and furnish samples to WL/MNME for verification.
5. Modify product, if needed, to correct problems encountered by WL/MNME.
6. Commercialize and transfer technology
    A. Explore transfer methods
    B. Plan commercialization
    C. Document commercial applications and possible Phase III SBIR program
    D. Recommend transfer methods

MACH I completed the program on schedule. Of 9 specific objectives included in the six tasks, 8 were achieved.

ACCOMPLISHMENTS

The literature review provided valuable insight concerning the multiple mechanisms by which waxes desensitize explosives. This guided MACH I's selection of candidate waxes for work under this program and for future R&D by WL/MNME.

MACH I developed mechanistic reasoning and laboratory procedures for selection and testing candidate ingredients. Of particular importance was identification and application of nonexplosive simulants for TNT. Proper choice of wax or wax substitute offers the prospect of enhancing specific mechanisms of desensitization. Thus explosive compositions could be tailored for differing applications (e.g., shells vs. bombs) and explosive performance (e.g., sensitivity to the fuze and yield). Synthetic wax substitutes offer much greater flexibility of formulation than do microcrystalline petroleum waxes.

Polar wax substitutes were identified as particularly promising in respect to:

- Melting point
- Emulsifiability
- Capability of wetting, dispersing, and coating explosive fillers, thereby:
  - Providing greater desensitization and
  - Shortening processing time
- Probable reduced tendency to be exuded from finished explosive
- Economy
- Reproducible physical and chemical properties
- Long term availability

By far the greatest challenge in this program was development of an effective emulsifier for a given candidate wax or wax substitute. Using both literature and extensive in-house experience, MACH I selected surface-active agents (surfactants) expected to excel as emulsifiers/dispersants for microcrystalline petroleum wax, synthetic polyethylene wax, and other wax substitutes. Of many candidate nonexplosive matrices two proved to be satisfactory simulants for TNT in emulsion stability tests. Standard laboratory test procedures were developed for ranking candidate surfactants and for demonstrating complete desensitizing formulations.

On the basis of laboratory tests MACH I selected and provided specimens of 16 wax substitute emulsifier combinations to WL/MNME for evaluation with TNT. WL/MNME found 11 of these to be compatible (by DSC) and to provide acceptable emulsions.

Plans have been made for commercialization and technology transfer under a Phase III program.

MAJOR ACHIEVEMENTS

Novel, promising desensitizing systems were furnished to WL/MNME for evaluation with TNT. Their findings with live explosive, which verify MACH I's laboratory results, include:

- Demonstration of chemical compatibility with TNT by DSC
- Demonstration of miscibility with molten TNT and acceptable stability of the resultant emulsion
- Optical and SEM photomicrographs of simulant or explosive compositions that confirm efficient coating of TNT crystals

Prior efforts failed to yield a satisfactory emulsifier for the candidate wax substitute Polywax 600, an otherwise very attractive synthetic polymer. However, under the present program MACH I attained this challenging goal by adding 10-15% of a styrene-butadiene block copolymer coupling agent to Ganex WP-660, a polyvinylpyrrolidone resin surfactant. The laboratory demonstration of emulsion stability has been confirmed by WL/MNME using molten TNT.

Under Phase I of the present program MACH I and WL/MNME showed that Ganex resin surfactants yield stable emulsions with molten TNT and microcrystalline wax (Indramic 170C, Indramic 800 and others) without the need for troublesome nitrocellulose and lecithin. An objective of the Phase II program was to find a back-up surfactant for the promising Ganex family in this specific application. However, despite testing of many varied commercial surfactants and specially synthesized candidates, a satisfactory back-up has not been found. Nevertheless, the Ganex family remains very promising, and a back-up may not be required.

The Ganex surfactants are unique and excellent emulsifiers for microcrystalline petroleum wax. In addition to emulsifying, the Ganex surfactants:

- Wet particles
- Disperse particles
- Coat particles
- Reduce friction
- Reduce viscosity
- Reduce air entrapment and thus increase density
- Increase desensitization
- Increase production rate of melt-cast TNT and PBX explosives.

These benefits have been demonstrated by:

- Optical photomicrographs of Ganex WP-660/wax/2,4-DNT
- SEM photomicrographs showing that at about one-half the concentration Ganex WP-660 outperforms lecithin in an Octol (HMX/TNT)/aluminum/wax composition, and nitrocellulose and lecithin in a TNT/Composition D-2 wax containing composition.

- A ten-fold reduction in viscosity of modified AFX-931 general purpose PBX bomb explosive at Atlantic Research Corporation using only 0.2% Ganex V-216 or Ganex V-220.
- Solution of multiple problems plaguing development of AFX-644 by replacing nitrocellulose and lecithin in Composition D-2 with Ganex WP-660. Development of the improved composition had progressed to testing of 500 lb. bombs in mid-1993.
- Altered critical diameter of explosive compositions. This feature may be fundamentally important.

Used with or without a desensitizing wax, the Ganex resin surfactants are expected to be effective processing aids for a wide spectrum of munitions and manufacturing processes.

RECOMMENDATIONS

DOD should build on the achievements of the present work by establishing a program to:

- Exploit more fully the following important benefits offered by top quality emulsifiers, such as the Ganex resin family:
    - Better wetting
    - Better dispersion
    - Reduced viscosity
    - Nonexplosive classification
- Replace today's undependable and inconsistent desensitizing wax with synthetic substitutes that offer:
    - Superior desensitization
    - Improved physical stability of finished explosive
    - Dependable, controlled properties
    - Assured availability

The program should include appropriate application of the superior emulsifiers and wax substitutes to:

- All melt-cast explosive systems such as Compositions B, HBX-1, D-2, and H-6
- Batch- and continuously-mixed PBX systems
- Other anhydrous munitions mixing processes, including those for manufacture of ammunition, bombs, missiles, projectiles, pyrotechnics, demolition charges, and special purpose devices.

The program should investigate the fundamental mechanisms associated with GANEX resin effectiveness in desensitizing energetic systems. The present work clearly identified the GANEX utility in this regard, but also indicated formulation constraints relevant to use concentration effectiveness. When the fundamental model of GANEX resin performance is understood, the unique contribution of additive levels of this to various energetic systems could be optimized. A new control mechanism for formulating and compatabilizing a wide variety of explosives, propellants, and pyrotechnics would hence be available.

MACH I, Inc. has demonstrated the qualification to serve as contractor for such a program and to transfer the related technology to the public and private sectors. Beyond the technology generated under the present program, MACH I has:

- Extensive expertise in the field of surfactants.
- Experience in the field of energetic compositions (explosives, propellants, pyrotechnics).
- Outstanding marketing capabilities for promoting innovative concepts and products.
- A strong commitment to sell the technology and Military Aerospace CHemical Ingredients.

MACH I recommends and has requested WL/MNME assistance during its SBIR Phase III Commercialization efforts by preparing a paper for publication and joint presentation with MACH I which details WL/MNME work and research and development conclusions on the utility of GANEX resins in TNT based bomb desensitizing formulations. Targeted audiences for these presentations include:

- Present a short paper to the Explosives and Propellants Subgroup Meeting as was done at the meeting at Holston Army Ammunition Plant on August 25, 1993.
- Present a paper at a JANNAF Interagency Propulsion Committee Meeting on the subject of manufacturing technology for insensitive munitions (IM), propellants and explosives
- ADPA Meeting in 1995.
- ICT Annual Conference in 1995.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

LIST OF FIGURES

LIST OF FIGURES (continued)

LIST OF FIGURES (continued)

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF TABLES (continued)

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LIST OF ABBREVIATIONS AND ACRONYMS

2,4-DNT	2,4-Dinitrotoluene, nonexplosive simulant for TNT
AFX-644	30% TNT, 40% NTO, 20% Al, 10% Wax and Emulsifier
AFX-931	32% RDX, 37% Ammonium Perchlorate, 15% Al, 8% Poly bd R45HT 7% Sunthene 420, 1% IPDI
APP	Amorphous Polypropylene
ARC	Atlantic Research Corporation
ARDEC	Armaments Research, Development and Engineering Center, Picatinny Arsenal, Dover, NJ
ASTM	American Society For Testing Materials
Composition B	39.5% TNT, 59.5% RDX, 1.0% Wax
Composition D2	84% Wax, 14% Nitrocellulose, 2% Lecithin
cP	Centipoise
DOD	Department of Defense
DSC	Differential scanning calorimetry (or calorimeter)
DTIC	Defense Technology Information Center
F-T	Fischer-Tropsch
FDA	Food And Drug Administration
fps	Foot pound second
gc	Gas chromotography
glc	Gas-liquid chromatography
HBX-1	38% TNT, 40% RDX, 17% Al, 5% Wax
HERD	High Energy Research & Development (at Eglin AFB)
HLB	Hydrophile-lipophile balance
HMX	1,3,5,7-tetranitro-1,3,5,7-tetrazocyclooctane
ICT	Fraunhofer-Institut Für Chemische Technologie
IM	Insensitive munitions

LIST OF ABBREVIATIONS AND ACRONYMS (continued)

IPDI	Isophorone Diisocyanate
ISP	International Specialty Products
NE	Nitroethane, a nonexplosive simulant for TNT
NPRA	National Petroleum Refiners Association
NSWC	Naval Surface Warfare Center
NTO	3-Nitro-1,2,4-triazole-5-one
Octol	75% HMX, 25% TNT
PAO	Poly(α-olefin)
PBMA	Polybutadiene/maleic anhydride
PBX	Plastic Bonded Explosive
PVP	Polyvinylpyrrolidone
QPL	Qualified Products List
R&D	Research and development
RDX	1,3,5-trinitro-1,3,5-triazocyclohexane
SBIR	Small Business Innovative Research
SEM	Scanning Electron Microscopy
SIC	Standard Industrial Code
SMA	Styrene-maleic Copolymer Half Esters
TAPPI	Technical Association of Pulp and Paper Industry
TEA	Triethanolamine
TNT	2,4,6-Trinitrotoluene
TNTO	A combination of TNT and NTO
TPP	Triphenylphosphate
USP	United States Pharmacopeia
VP	Vinyl Pyrrolidone
WL/MNME	Wright Laboratory, Armament Directorate, Energetic Materials Branch

LIST OF TRADENAMES

Trade Names	Description	Manufacturer
AC 400A Copolymer	Ethylene-Vinyl Acetate Copolymer	Allied Signal Inc.
AC 5120	Ethylene-Acrylic Acid Copolymer	Allied Signal Inc.
AC 617	Polyethylene Wax	Allied Signal Inc.
AC 656	Oxidized Polyethylene Wax	Allied Signal Inc.
Aclyn 285A	Ethylene-Acrylic Acid Sodium Ionomer	Allied Signal Inc.
Aclyn 295A	Ethylene-Acrylic Acid Zinc Ionomer	Allied Signal Inc.
Acryloid 947T	Polymers Grafted With Vinyl Pyrrolidone	Rohm & Haas Co.
Acryloid 956	Polymers Grafted With Vinyl Pyrrolidone	Rohm & Haas Co.
Acryloid B67	Polyisobutyl Methacrylate	Rohm & Haas Co.
Acryloid DM-55	Polyacrylate	Rohm & Haas Co.
Aerosol OT100	Sodium Di(2-ethylhexyl)sulfosuccinate	American Cyanamide
Aerosol TR70	Sodium Ditridecylsulfosuccinate	American Cyanamide
Alkaterge C	Octadecyl Oxazoline	Angus Chemical
Antiterra 204	Polymeric Carboxylic Acid Salt Of Polyamines-amides	BYK Chemie USA
Antiterra U	Polymeric Ester Salt Of Polyamines-amides	BYK Chemie USA
Arconate	Propylene Carbonate	ARCO Chemical
Aristonate H	Sodium C23 Alkylbenzene Sulfonate	Pilot Chemical Co.
Aristonate L	Sodium C18 Alkylbenzene Sulfonate	Pilot Chemical Co.
Aristonate M	Sodium C20 Alkylbenzene Sulfonate	Pilot Chemical Co.
Armac HT	Hydrogenated Tallow Amide	AKZO Chemical
ARMEEN 12D	Dodecylamine	AKZO Chemical
ARMEEN 18D	Octadecylamine	AKZO Chemical
ARMEEN DMOD	Oleyl-dimethylamine	AKZO Chemical
ARMEEN M2C	Dicocoalkyl-methylamine	AKZO Chemical
ARMEEN OL	Oleylamine	AKZO Chemical
Basic Barium Petronate	Barium Petroleum Sulfonate	Witco Chemical Co.
Biosoft S-100	Dodecylbenzenesulfonic Acid	Stepan Chemical
Brij 96	Polyoxyethylene Oleyl Ether	ICI Americas Inc.
Calcium Petronate 25CG	Calcium Oberbased Petroleum Sulfonate	Witco Chemical Co.
Centophase HR2B	Low Viscosity Fluid Lecithins	Central Soya
Centrol 1PUB	Lecithin From Soybean Oil	Central Soya
Centrolene A	Water Dispersable Lecithin	Central Soya
Ceramer 1608	Maleic Anhydride Adducts Of Polyethylene	Petrolite Corp.
Ceramer 67	Maleic Anhydride Adducts Of Polyethylene	Petrolite Corp.
Duomeen T	N-Tallow-1,3-diaminopropane	AKZO Chemical
Duomeen TDO	N-Tallow-1,3-diaminopropane Dioleate	AKZO Chemical
Eastoflex D139	Propylene-butene Copolymer	Eastman Chemical
Eastoflex D147	Propylene-ethylene-butene Terpolymer	Eastman Chemical
Eastotac H-1006	Hydrocarbon Resin	Eastman Chemical
Elvax 310	Ethylene-vinyl Acetate Copolymer	DuPont Co.
Elvax 40W	Ethylene-vinyl Acetate Copolymer	DuPont Co.
Elvax 500	Ethylene-vinyl Acetate Copolymer	DuPont Co.
Elvax 660	Ethylene-vinyl Acetate Copolymer	DuPont Co.
EMAC SP 2220	Ethylene-methyl Acrylate Copolymer	Chevron Chemical
EMAC SP 2255	Ethylene-methyl Acrylate Copolymer	Chevron Chemical

LIST OF TRADENAMES (continued)

EMAC SP 2260	Ethylene-methyl Acrylate Copolymer	Chevron Chemical
Epolene E-14	Oxidized Polyethylene Polymer	Eastman Chemical
Epolene E-15	Oxidized Polyethylene Polymer	Eastman Chemical
Epolene N34	Polyethylene Wax	Eastman Chemical
Ethoduomeem T/12	Ethoxylated N-tallow-1,3-diaminopropane	AKZO Chemical
Ethoduomeem T/25	Ethoxylated N-tallow-1,3-diaminopropane	AKZO Chemical
Flexomer DEFD 1015	Ethylene-olefin Copolymer	Union Carbide Corp.
Ganex® V-216 resin	Alkyl Polyvinylpyrrolidone Resin	ISP
Ganex® V-220 resin	Alkyl Polyvinylpyrrolidone Resin	ISP
Ganex® WP-660 resin	Alkyl Polyvinylpyrrolidone Resin	ISP
Hamposyl C	N-Cocoylsarcosine	Hampshire Chemical
Hamposyl L95	Sodium N-Lauroylsarcosinate	Hampshire Chemical
Hamposyl O	N-Oleoylsarcosine	Hampshire Chemical
HEP	N-(2-Hydroxyethyl)-2-pyrrolidone	Rhone-Poulenc Inc.
Hi Tech 644	Polymers With Succinimide Fuctionality	Ethyl Corp.
Hi Tech 646	Polymers With Succinimide Fuctionality	Ethyl Corp.
Hi Tech 648	Polymers With Succinimide Fuctionality	Ethyl Corp.
Hybase C-400G	Calcium C22 Alkylbenzene Sulfonate Overbased	Witco Chemical Co.
Hybase M-400TG	Magnesium Petroleum Sulfonate, Overbased	Witco Chemical Co.
Hystrene 3695	Dibasic 36 Carbon Carboxylic Acid	Witco Corp.
Igepon T77	Sodium N-Oleoyl-N-methyltaurate	Rhone-Poulenc, Inc.
Indulin W	Neutralized Aminolignin Sulfonic Acid	Angus Chemical
Jayflex DTBD	Ditridecyl Phthalate	Exxon
Kenamide E	Erucamide	Witco Corp.
Kenamide S	Stearylamide	Witco Corp.
Kenamide S180	Stearyl Stearamide	Witco Corp.
Kenamide S221	Erucyl Stearamide	Witco Corp.
Kenamine DD3680	Dimer Diamine	Witco Corp.
Kenamine DP3695	Dimer Diprimary Amine	Witco Corp.
Kenrich KR46b	Organic Titanate	Kenrich Inc.
Kenrich KR55	Organic Titanate	Kenrich Inc.
Kenrich LICA 12	Organic Titanate	Kenrich Inc.
Kenrich LICA 38	Organic Titanate	Kenrich Inc.
Kenrich LICA 44	Organic Titanate	Kenrich Inc.
Kenrich NZ9	Organic Zirconate	Kenrich Inc.
Kenrich NZ12	Organic Zirconate	Kenrich Inc.
Kraton D1101	Butadiene-styrene Block Copolymer	Shell Chemical Co.
Kraton G1650M	Ethylene-butylene-styrene Block Copolymer	Shell Chemical Co.
LOA 565	Aminopolyester Polymer	DuPont Co.
Lubhophos LF200	Partial Phosphate Ester Of Dodecylphenol	Rhone-Poulenc Inc.
Lubrizol 2633	Polyolefin Amide Alkeneamine	Lubrizol Corp.
Lubrizol OS22777	Copolymer Ester	Lubrizol Corp.
Lubrizol OS47550	Polyolefin Amino-ester Salt	Lubrizol Corp.
Lubrizol OS87440	Polyolefin Amide Alkeneamine	Lubrizol Corp.
Monowet MT80H2W	Sodium Ditridecylsulfosuccinate	Mona Industries
Neofat 8S	Caprylic Acid	AKZO Chemical
Nipol 1312	Liquid Butadiene-Acrylonitrile Copolymer	Zeon Chemicals, Inc.
Neutral Barium Petronates	Barium Petroleum Sulfonate	Witco Chemical Co.

LIST OF TRADENAMES (continued)

Nipol 1312LV	Liquid Butadiene-Acrylonitrile Copolymer	Zeon Chemicals, Inc.
Nipol DN601	Preplasticized Nitrile Rubber	Zeon Chemicals, Inc.
Paraloid K120N	Methyl Methacrylate-Ethyl Acrylate Copolymer	Rohm & Haas
Paranox 106	Nitrogen Containing Polymer	Exxon Corp.
Paranox 147	Nitrogen Containing Polymer	Exxon Corp.
PBMA-10	Polybutadiene-Maleic Adduct	Ricon Inc.
Petrolite C-7500	Oxidized Polyethylene	Petrolite Corp.
Petrolite C-8500	Oxidized Polyethylene	Petrolite Corp.
Petrolite C-9500	Oxidized Polyethylene	Petrolite Corp.
Petrolite Cp-7	Ethylene Copolymer	Petrolite Corp.
Petronate 540	Sodium Petroleum Sulfonate	Witco Chemical Co.
Petronate HL	Sodium Petroleum Sulfonate	Witco Chemical Co.
Pluronic F68	Block Propyleneoxide-Ethyleneoxide Copolymer	BASF Corp.
Pluronic L61	Block Propyleneoxide-Ethyleneoxide Copolymer	BASF Corp.
Polywax 600	Polyethylene Wax	Petrolite Corp.
Propameen T/12	Propoxylated Diamine	AKZO Chemical
Rhodafac RM510	Partial Phosphate Ester Of Dinonylphenol	Rhon-Poulenc Inc.
Rhodofac RE610	Partial Phosphate Ester Of Nonylphenol	Rhone-Poulenc Inc.
Rhodofac RS710	Partial Phosphate Ester Of Tridecyl Alcohol	Rhone-Poulenc Inc.
Santicizer 148	Isodecyl Diphenyl Phosphate	Monsanto Company
Silwet L7001	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L7210	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L7500	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L7602	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L7604	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L7622	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L77	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
Silwet L772	Polyalkoxylated Dimethylsiloxane	Union Carbide Corp.
SMA 1000	Stryene-maleic Copolymer	Atochem N. A.
SMA 1440	Stryene-maleic Copolymer Ester	Atochem N. A.
SMA 17352	Stryene-maleic Copolymer Ester	Atochem N. A.
SMA 2625	Stryene-maleic Copolymer Ester	Atochem N. A.
SMA 3000	Stryene-maleic Copolymer	Atochem N. A.
Solsperse 13345	Polymeric Fatty Ester	ICI Amerigas Inc.
Solsperse 17000	Quaternary Polymer	ICI Amerigas Inc.
Solsperse 20000	Polyamine	ICI Amerigas Inc.
Solsperse 24000	Polymeric Agent	ICI Amerigas Inc.
Solsperse 5000	Blue Pigment Derivative	ICI Amerigas Inc.
Solsperse 22000	Yellow Pigment Derivative	ICI Amerigas Inc.
Span 85	Sorbitan Trioleate	ICI Americas Inc.
Sunthene 420	Napthenic Process Oil	Sun Oil Co.
Surphadone LP100	N-Octyl Pyrrolidone	ISP
Surphadone LP300	N-Dodecyl Pyrrolidone	ISP
Telura 343	Napthenic Process Oil	Exxon
Triamine T	N-Tallow Alkyldipropylene Triamine	Akzo Chemical

LIST OF TRADENAMES (continued)

Trilene CP80	Ethylene-Propylene Liquid Copolymer	Uniroyal Chemical Co.
Trilene MB	Plasticized Terpolymer	Uniroyal Chemical Co.
Triphenyl phosphate		Monsanto Company
Triton X15	Octylphenol Polyether Alcohols	Union Carbide Corp.
Triton X45	Octylphenol Polyether Alcohols	Union Carbide Corp.
Unilin 425	Saturated Long Chain Linear Alcohols	Petrolite Corp.
Unilin 550	Saturated Long Chain Linear Alcohols	Petrolite Corp.
Unilin 700	Saturated Long Chain Linear Alcohols	Petrolite Corp.
Unithox 420	Ethoxylated Long Chain Alcohols	Petrolite Corp.
Unithox 450	Ethoxylated Long Chain Alcohols	Petrolite Corp.
Unithox 480	Ethoxylated Long Chain Alcohols	Petrolite Corp.
Unithox 520	Ethoxylated Long Chain Alcohols	Petrolite Corp.
Unithox 550	Ethoxylated Long Chain Alcohols	Petrolite Corp.
Vybar 103	Highly Branched Olefin Polymer	Petrolite Corp.
Witconate P1059	Branched Dodecylbenzenesulfonic Isopropylamine Salt	Witco Corp.
Zetpol 20001	Hydrogenated-Butadiene-Acrylonitrile Copolymer	Zeon Chemicals, Inc.

SECTION I

INTRODUCTION

1. BACKGROUND

For the past half-century waxes and related materials have served as desensitizers in a variety of cast explosives to guard against accidental initiation by shock, impact, or other stimuli. Most of these desensitizers are derived from natural products and they suffer from several serious limitations:

- Undependable physical/chemical properties
- Unpredictable cost
- Uncertain supply.

A wax or wax-like substance alone performs poorly. Achievement of acceptable processing and properties of the cast explosive requires inclusion of emulsifiers and modifiers, for example lecithin (a natural substance of uncertain and variable composition) and nitrocellulose (an explosive that requires special handling and sometimes impairs aging stability). A widely used formulation containing these additives (Composition D-2 MIL-C-1816A Wax, Desensitizing) presents a variety of problems including:

- Varying viscosity, hence occasional processing difficulty
- Defects in the casting
- Fouling of processing equipment
- Gassing of the cast explosive
- Classification as an explosive, which complicates storage and handling.

Under Phase I of the present program (Wright Laboratory Air Force Contract F08630-91-C-0029) MACH I, Inc. evaluated a wide variety of surface active agents (surfactants) as candidate processing aids for nitramine-containing TNT melt-cast explosives and plastic-bonded explosives (PBXs). Just before the contract started, WL/MNME encountered several serious problems associated with D-2 desensitizing wax used in the AFX-644 TNT melt-cast system: variable viscosity of the melt, deposition of nitrocellulose on the mixer walls, as well as both physical and chemical instability of the product. Using an explosive-free simulant formulation, MACH I identified a promising family of polyvinylpyrrolidone resin emulsifiers, Ganex WP-660, V-216 and V-220. Investigators at WL/MNME demonstrated that the Ganex additives yielded stable emulsions with molten TNT and microcrystalline waxes without the need for either nitrocellulose or lecithin. Using a different explosive-free simulant formulation, MACH I selected six of the most promising surfactant systems for testing by subcontractor Atlantic Research Corp.(ARC) in a challenging variant of the plastic-bonded explosive AFX-931. This effort demonstrated that Solsperse 13345, a polymeric surfactant, rivaled lecithin.

The properties and especially the supply of suitable microcrystalline waxes are variable and uncertain. The Air Force needs a substitute with constant, reliable properties and availability. These requirements are best met by either a pure chemical compound or a synthetic substance prepared by precisely controlled means from abundant starting materials.

2. TECHNICAL OBJECTIVES OF THIS PROGRAM

Phase II Research (Wright Laboratory Air Force Contract F08630-92-C-0058), "Surfactants and Desensitizing Wax Substitutes for TNT-Based Systems" extended the Phase I effort and encompassed two primary objectives and seven additional ones.

The two primary objectives are:
- develop an emulsifier to provide satisfactory emulsion stability for synthetic polyethylene wax, Polywax 600, in nitroethane simulant for TNT.
- develop a good emulsifier for microcrystalline wax Indramic 170C, of different chemical composition than Ganex resin, as a backup for Ganex resin.

In the order of importance, the additional objectives were:

1.) Assist WL/MNME in overcoming any unforeseen performance characteristic or handling problems associated with using or specifying MACH I recommended emulsifier formulated into standard explosives.

2.) Develop wax substitutes for use in TNT melt cast systems that meet performance criteria consisting of:
    - miscibility (emulsion stability)
    - stability (thermal)
    - compatibility
    - desensitizing effectiveness
    - long term supply
    - long term consistent composition
    - long term reliable performance

3.) Prepare a market study to provide an up-to-date review of the overall wax industry in the United States and how it relates to the use of desensitizing waxes for explosives.

4.) Determine the mechanisms for desensitization of explosives with wax by a literature review and develop criteria for selection of waxes and wax substitutes.

5.) Identify the process and methodology for selection of improved explosive matrix/wax/emulsifier systems.

6.) Develop an emulsifier to provide good emulsion stability with nitroethane simulant.

7.) Develop plans for Phase III commercialization and technology transfer.

These objectives are to provide guidance for the experimental work in this program and for future work by WL/MNME.

3. SCOPE OF THIS PROGRAM

This two-year, Phase II program consisted of the following six tasks, each of which is reported in one or two of the Sections of this report.

Task 1. Review the literature for use of waxes in military applications, particularly TNT melt casting.

A. History
  1. Properties
  2. Supply and availability
  3. Sources
  4. Use

B. Develop selection criteria, and identify properties required for military applications.
  1. Growth and exudation
  2. Melt point and softening point
  3. Miscibility
  4. Desensitizing effectiveness
  5. Physical properties
  6. Compatibility

Task 2. Identification of process/methodology for selection of explosive matrix/wax/emulsifier systems.

A. Stability
B. Miscibility
C. Compatibility
D. Homogeneity

Task 3. Identification and selection of waxes, wax substitutes and surfactants for a given matrix (TNT).

A. Matrix
  1. TNT and TNT substitutes
  2. Others to be determined by WL/MNME

B. Waxes
   1. Microcrystalline
   2. Polyethylene
   3. Others to be determined by WL/MNME and/or MACH I

C. Wax substitutes: a minimum of four suitable candidates to be determined by MACH I.

D. Surfactants: a minimum of one suitable for each system, to be determined by MACH I.

Task 4. Evaluate candidate systems and provide samples of wax substitutes and surfactants for verification and evaluation in target explosive matrix for the following properties.

A. Miscibility
B. Stability
C. Compatibility

Task 5. Modify product, if needed, to correct problems encountered by Air Force.

Task 6. Phase III commercialization and transfer technology plans.

A. Explore methods to transfer the technology developed under this Phase II Small Business Innovative Research (SBIR) program.

B. Plan for the commercialization of any new or innovative technology resulting from this Phase II SBIR program.

C. Document commercial applications of the technology as well as possible follow-on Department of Defense (DOD) Phase III efforts.

D. Recommend methods to pursue the transfer of the technology to the private or public sector.

SECTION II

MARKET REVIEW OF WAX AND WAX SUBSTITUTES

1. SUMMARY AND CONCLUSIONS

To fulfill the requirements of Task 1 of this program, a complete market study of the U.S. wax industry was completed. This included supply and demand for all major waxes including petroleum, mineral, vegetable, animal and synthetic waxes.

Review of the military requirements for desensitizing waxes indicates a need of 50,000 pounds per year during extended peace times, 500,000 pounds per year for a limited war like the Persian Gulf campaign and several million pounds per year for an extended war like the Vietnam conflict.

Many different chemical types of synthetic wax substitutes were reviewed for new candidates with a potential to meet specification MIL-W-20553D. A melting range of 70-100°C was used for general screening. A number of products were identified to consider in the experimental work of this program. One of the most promising classes is the low molecular weight polyethylene homopolymers. A second, and somewhat related class, includes copolymers of ethylene and/or propylene with butene, hexene, vinyl acetate or methyl acrylate. Alpha olefins of $C_{30}+$ chain length also show promise, as do fatty amides.

From a technical viewpoint, the montan waxes and Fischer-Tropsch waxes are good desensitizers. However, the overriding consideration of availability during a war is a serious problem.

Petroleum waxes will continue to dominate the U.S. wax industry. Microcrystalline waxes should still be available but at a higher price. Problems of obtaining specification grade microcrystalline waxes will be aggravated and more frequent due to environmental constraints on refineries. The volume of wax required that nominally is qualified should be available, but when needed, may not qualify based on past history.

A number of advantages favor the development of new synthetic desensitizing wax substitutes. They are available in significant volume with consistent composition and reliable performance over the long term.

2. INTRODUCTION

The objective of this market study is to provide an up-to-date review of the overall wax industry in the United States and how it relates to the use of desensitizing waxes for explosives. More specifically, it helped guide MACH I's experimental effort on this program and will be useful for future R&D by WL/MNME on cast TNT and related explosives. Supply, demand, availability and prices of most waxes are listed with discussions of the many developments that will affect their future supply and demand.

One of the greatest problems in procurement of waxes for the military has been the lack of continuous supplies of qualified products once they were on the Qualified Products List (QPL). Factors that have caused this are also discussed.

Efforts have been directed toward finding new waxes or wax substitutes to consider for use in this program in place of the microcrystalline waxes, montan waxes and low molecular weight polyethylene waxes already under consideration.

3. DESENSITIZATION OF EXPLOSIVES BY USE OF WAX

A comprehensive literature search was made by the Defense Technology Information Center (DTIC) for this program. The search provided an excellent review of the history of desensitizing waxes from the early use of beeswax followed by petroleum waxes during World War II. It covered work on mechanisms determining what makes a good desensitizing wax. Much work has been reported on wax substitutes such as synthetic polymers, fatty amides and other synthetic waxy compounds as replacements for naturally occurring waxes. This review and references have been extremely helpful in the conduct of Task 1 as well as the experimental work of this program.

The current status of microcrystalline petroleum waxes is much the same as reported in 1975 by Kemp and Anthony of the Naval Surface Weapons Center as follows (Reference 5):

> "Microcrystalline waxes, particularly the Grade A type, are very minor by-products of the oil industry and are, therefore, subject to wide fluctuations in availability depending upon processing practices which, perforce, must be geared to demands for the principal products, gasoline and fuel oil. Petroleum waxes of all kinds account for only 0.1% of the production of the industry. In 1974, according to U.S. Bureau of Mines estimates, U.S. production of all types of petroleum waxes was 6,929,000 barrels (280 lb/bbl) of which only 16.4% was microcrystalline. Industry spokesmen estimate that not more than 20% of the microcrystalline production could be classified as Grade A. Calculations based on these estimates reveal that Grade A microcrystalline wax amounts to less than 0.003% of the total, indeed a minor product of the petroleum industry."

It is important to understand how the very specific use of desensitizing waxes in military explosives fits into the overall wax industry in the United States. Recent developments and changes occurring in the petroleum industry, especially environmental constraints, will affect the future availability of petroleum waxes. Several opportunities exist for the development of new synthetic wax substitutes.

4. WAXES DERIVED FROM NATURAL SOURCES

a. Petroleum Waxes

(1) General Information

Waxes derived from petroleum account for about 97% of the total U.S. market for waxes. The processing of crude oil by petroleum companies gives two types of waxes - paraffin and microcrystalline. The amount and physical properties of waxes recovered from crude oil vary greatly with the source of crude oil. Some crudes contain little wax. The U.S. crudes from Pennsylvania and the midcontinent areas contain high concentrations.

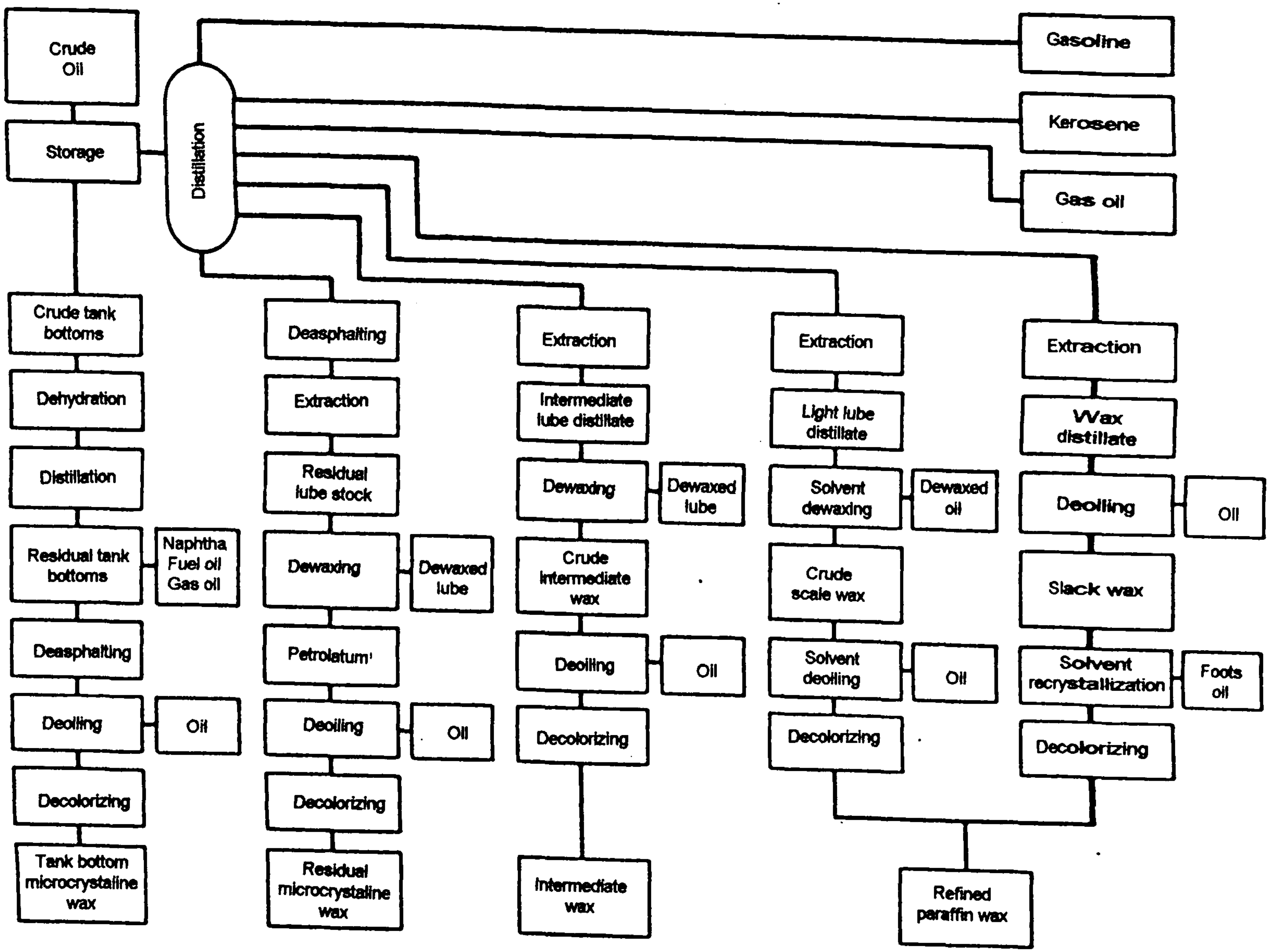
The paraffin waxes, obtained by dewaxing the distillate for lube oil bases, are long-chain (C_{20} to C_{35}) paraffins. They are primarily straight chain hydrocarbons but may contain from 10-15% of slightly branched isoparaffins. Paraffin waxes have a large plate-crystal structure. Melting points of paraffin waxes can range from 110°F to 160°F. Three industrial grades are normally supplied: (a) 125-135°F, (b) 140-145°F and (c) 150-155°F. Oil content is usually under 0.5%, and they are usually white and translucent.

Microcrystalline waxes are recovered from the residues of a crude oil refinery. (Petroleum tars and asphalt are also recovered from the same residues.) Microcrystalline waxes may vary in color from white to yellow, amber, or even black. They are hydrocarbons with higher molecular weights than paraffin waxes and contain a much greater concentration of branched chains. At first they were thought to be amorphous, but microscopic examination showed them to consist of very fine needle-like crystals - hence the term "microcrystalline" was adopted. Melting ranges extend from 140°F to over 200°F.

Some of the higher melting microcrystalline waxes are obtained from crude oil before it is distilled at a refinery. The so called "tank waxes" separate as crystals or solids directly from crude oil in storage. These are collected and refined into purer waxes. For example, Petrolite is known to purchase these crude waxes from petroleum companies for processing into high-melting microcrystalline waxes.

Petrolatum is removed from short residue slack wax prior to the recovery of microcrystalline waxes. A wide variety of soft grease-like waxes are marketed as petrolatums. These materials are wax-oil mixtures with oil content up to 25%.

The following flow chart (Figure 1), courtesy of the Petrolite Corp., outlines a typical refinery flow sheet and the sources of the various grades of waxes.



Courtesy of Petrolite Corporation

Figure 1. Refining of Petroleum Waxes

(2) Supply and Demand

The supply and demand data for petroleum waxes in the United States from the U.S. Department of Energy and Department of Commerce are shown in Table 1 (Reference 41). There has been only a small growth in the total demand over the last ten years. It is expected to grow at about the same rate in the future.

TABLE 1. PETROLEUM WAXES SUPPLY AND DEMAND 1982-1992
(Millions of Pounds)

	1982	1987	1988	1989	1990	1991	1992 est.
Production	1,456	1,666	1,753	1,764	1,755	1,872	1,850
Exports	77	211	276	264	320	346	306
Imports	168	191	207	207	179	174	236
Demand	1,547	1,646	1,684	1,707	1,614	1,700	1,780

(3) U.S. Capacities

The National Petroleum Refiners Association (NPRA) publishes an annual survey "Lubricating Oil and Wax Capacities of U.S. and Canadian Refineries." Table 2 shows results of the latest survey (1/1/92).

TABLE 2. NPRA ANNUAL SURVEY OF WAX CAPACITIES
UNITED STATES AND CANADA - 1/1/92
(Millions of Pounds)

Producers, USA	Column A	Column B	Column C
Amoco Oil Company	62	---	62
Ashland Petroleum Company	--	290	290
Chevron, U.S.A., Inc.	127	496	623
Cit-Con	120	83	203
Conoco	31	---	31
Exxon Company, U.S.A.	175	186	361
Lyondell Petrochemical Co.	---	103	103
Mobil Oil Co.	165	31	196
Pennzoil Products Company	145	42	187
Petrolite Corporations	42	31	73
Petrowax PA	196	31	227
Quaker State Oil Refining Co.	---	52	52
Shell Oil Company	103	--	103
Star Enterprises	---	186	186
Sun Company, Inc.	83	217	300
Unocal	73	134	207
Witco Corporation	21	---	21
Total	1,343	1,882	3,225

TABLE 2 (continued)

Producers - Canada

Esso Petroleum Canada	---	290	290
International Waxes, Ltd.	104	---	104
Petro-Canada	---	104	104
Shell Canada Limited	---	135	135
Total	104	529	633

Column A – fully refined, crude scale and microcrystalline waxes
Column B – semi-finished, slack waxes and petrolatums
Column C – total (i.e., sum of Columns A and B)

Total wax capacity increased 190 million pounds during 1991. Petrowax added 82 million pounds for fully refined waxes. Lyondell, Houston added 62, Petrowax added 21 and Exxon, Baton Rouge added 20 million pounds of semi-finished products.

Lube oil capacity, however, was reported to be down 4.5% from January 1, 1991 and down 10.6% for the last decade. Reduction last year was mainly due to shut-down of Sun Oil's Marcus Hook lube capacity in April 1991.

While these capacities are the official ones, industry sources say that actual capacities may vary substantially over the year due to operating changes made at each refinery. However, the trend to lower lube oil capacity and higher wax capacity appears to be permanent.

(4) U.S. Refinery Production of Refined Products

Table 3 shows the U.S. production of refined products by U.S. refineries since 1974. Gasoline production has leveled out using about 52% of crude consumption over the last five years, down from over 55% in the early 1980s. Lubricant production in 1991 declined 7% from 1990 and is 20% below the peak in 1979. Petroleum wax production at 6.69 million bbl in 1991 was about the same as 1974-79 and up from a low of 5.2 million bbl in 1982. Wax production in 1991 was 0.13% of crude consumption and 11.7% of lubricant production.

TABLE 3. U.S. PRODUCTION OF PETROLEUM REFINED PRODUCTS
(Billions of Barrels per Year, MM bbl)

	Crude Oil,	Gasoline		Lubricants		Waxes	
Year	MM bbl	MM bbl	%	MM bbl	%	MM bbl	%
1974	4,428	2,386	53.8	70.7	1.59	6.91	0.16
1979	5,336	2,567	48.0	71.0	1.33	6.89	0.13
1980	4,921	2,400	48.7	65.1	1.32	6.32	0.13

TABLE 3 (continued)

1981	4,551	2,405	52.8	60.6	1.33	6.94	0.15
1982	4,298	2,387	55.5	51.6	1.20	5.20	0.12
1983	4,265	2,417	56.6	53.8	1.27	5.54	0.12
1984	4,396	2,493	55.5	58.3	1.32	5.38	0.12
1985	4,381	2,465	56.9	53.0	1.21	5.45	0.12
1986	4,639	2,496	53.1	53.2	1.19	5.70	0.12
1987	4,692	2,526	53.2	61.6	1.31	5.88	0.12
1988	4,835	2,538	52.5	64.5	1.33	6.30	0.13
1989	4,891	2,541	51.9	59.7	1.24	6.22	0.13
1990	4,894	2,540	51.9	61.6	1.26	6.19	0.13
1991	4,853	2,547	52.4	57.0	1.17	6.69	0.13

Source: U.S. Department of Energy (Reference 8)

Some of the trends that will affect the future production of petroleum waxes are as follows:

(a) Lubricant production is declining, which will put pressure on supplies of raw materials for petroleum waxes.

(b) Since passage of the Amendment to the Clean Air Act in 1990, ten refineries have announced shut-downs with 290,000 barrels per day refinery capacity, seven others are looking for buyers, and some estimates indicate another 65 refineries are at risk of being closed due to the cost of complying with the Clean Air Act.

(c) Further treatment of residues by additional cracking to increase the yield of refined products will result in less residuals from which microcrystalline waxes are derived. *Hydrocarbon Processing* published a recent article on this subject by P. O'Connor (Reference 7).

(5) U.S. Markets

An estimate of the various markets for waxes in the United States is given in Table 4. Applications in the packaging industry account for much of the use, but a wide variety of other industries use substantial quantities. Petroleum waxes account for over 95% of the consumption.

The use of microcrystalline waxes to desensitize explosives is very small in relation to other uses. The *Encyclopedia of Explosives* (Reference 2) reported that in 1973 1.5 million pounds were used in Composition B. This large amount undoubtedly reflected Vietnam conflict needs. The current requirements, which appear to be much smaller, are given later in this report.

TABLE 4. U.S. CONSUMPTION OF ALL WAXES BY END USE
(millions of pounds per year)

Packaging	Annual Use
Flexible Packaging	200
Corrugated Containers	400
Cups and Containers	250
Folding Cartons	30
Non-Packaging	
Candles	200
Board Sizing	200
Tires and Rubber	80
Hot Melt Adhesives	100
Carbon Paper	20
Metal Working	60
Fireplace Logs	100
Cosmetics and Pharmaceuticals	60
Plastics	50
Crayons	20
Household, Waxes, Etc.	20
Miscellaneous	110
TOTAL	1,900

(6) U.S. Imports and Exports

In Table 1 (presented earlier) the last several years of imports and exports are listed with an estimate for 1992.

Total imports of petroleum waxes for the first six months of 1992 are valued at $29.4 million for an average price of 24.9 cents per pound. This is at an annual rate of 236 million pounds, up from 174 million pounds in 1991.

Exports of petroleum waxes for the first six months of 1992 totaled $55.1 million for an average price of 36.1 cents per pound. This is at an annual rate of 306 million pounds, down from 346 million pounds in 1991. It is interesting to note that this included 25 million pounds valued at 7.9 cents per pound in shipments to Germany from Puerto Rico in the first quarter of 1992.

(7) Prices of Petroleum Waxes

The *Chemical Marketing Reporter* September 14, 1992 prices for petroleum waxes in tank cars, refinery are shown in Table 5 (Reference 39). These are list prices only. Contract prices may vary as will those for individual products with special specifications or properties.

TABLE 5. U.S. PETROLEUM WAX PRICES
(tank cars at refinery)

Product	List Price (¢/lb)
Paraffin Slack Waxes	
5% Oil	19
12% Oil	21
20% Oil	16
Refined Paraffin Waxes	
127-130°F	25
130-135°F	37
140-145°F	37
150-156°F	37
Petrolatum	40
Microcrystalline Wax	
Coating, FDA	38 1/2
Laminating Grades, FDA	42 1/2

Source: Chemical Marketing Reporter, September 14, 1992

Prices in Table 6 were obtained from manufacturers for the specific petroleum waxes that either are, or might be used as, desensitizers. Several companies, e.g., Sun Oil and Exxon, no longer market waxes with melting points over 170°F.

TABLE 6. PRICES OF INDIVIDUAL PETROLEUM WAXES

Company & Product	Melting Point	Price (¢/lb)
Shell Oil Co.	183°F (D-87)	78.5 bulk
Shellwax 650		84.5 slabs truckload
Petrolite Corp.		
Be Square 185	192°F (D-127)	69.7 bulk
Be Square 195	199°F (D-127)	81.5 bulk
Petrolite C-700	199°F (D-127)	81.5 bulk
National Wax Co.	184°F (D-127)	52.5 bulk
Paxwax 680		70.5 slabs truckload
IGI Boler, Inc.		
Petrowax 9508	195°F (D-127)	80 bulk
H.B. Fuller		
HM-2826	177°F (drop point)	87 truckload
Industrial Raw Materials Corp.		
Indramic 170-C	182-6°F (D-127)	75 truckload
Indramic 800	181-192°F (D-127)	89.5 truckload

b. Natural Waxes Derived from Non-Petroleum Sources

(1) General Information

Beeswax was used over 6,000 years ago in Egypt for many different purposes. The term wax comes to us from the Anglo-Saxon "weax," the name given to material from the bee honeycomb. Today, the term wax has a much broader meaning and applies to all wax-like liquids or solids of either natural or synthetic origin. In general, waxes are plastic solids at room temperature and become low-viscosity liquids at moderately elevated temperatures. Nearly all uses of waxes depend on their physical, rather than chemical, properties.

In general, natural waxes vary substantially in chemical composition and quality. Vegetable waxes are usually produced in the wild and not by large scale cultivation. Although plants produce small amounts of waxes in their tissues, seeds and pollen, wax occurs more abundantly as excretions on leaves, stems or fruit, sometimes in amounts large enough to be commercially attractive. The composition of mineral waxes varies considerably from one deposit to another (e.g., peat, lignite, shale or coal) as also occurs with crude oil. Consequently, the properties of natural waxes vary greatly from one supplier to another.

Waxes are complex in chemical composition. They exhibit a large range of molecular weights and reactive functional groups, such as esters, acids or alcohols; or they may be simply hydrocarbons. Plant waxes are usually nonglyceryl esters of fatty acids and higher alcohols. Associated with these esters may be one or more fatty acids, alcohols, ketones, sterols, lactones or hydrocarbons. Mineral waxes, obtained by extraction from ligneous coals, contain wax esters, free acids, alcohols or ketones. Some yield hydrocarbons on destructive distillation.

The major commercially available natural waxes are from (a) insects: beeswax, (b) vegetables: carnauba, candelilla ouricury, and Japan waxes and (c) minerals: montan and ozokerite waxes.

Spermaceti wax from the sperm whale was a commercial product until adoption of the U.S. Endangered Species Act in the 1970's, which outlaws its sale and use. Petroleum waxes are classified as mineral waxes.

Numerous natural waxes are available in small amounts at high prices for special applications. Most attempts to produce larger quantities have failed.

The following list gives names of some of the less important natural waxes not listed above:

Esparto wax
Bamboo leaf wax
Hemp fiber wax
Jojoba wax
Castor wax
Sugar cane wax
Douglas fir bark wax
Rice bran wax
Ceresin waxes
Wool wax
Shellac wax

(2) Supply and Demand

Of the natural waxes (excluding petroleum waxes), beeswax is the largest item of commerce in the U.S. The annual U.S. consumption has averaged about 10 million pounds per year. Domestic production is about 8 million pounds per year with imports of nearly 2 million pounds per year.

Carnauba wax is the second most important. It is recovered from a particular palm tree in Brazil. The Brazilian government controls the marketing and price of carnauba wax. Imports into the U.S. average 7 million pounds per year.

Candelilla wax is used in cosmetics. It is extracted from shrubs in Mexico and to a lesser extent in the Big Bend area in Texas. The Mexican government controls the marketing and pricing of candelilla wax. About 0.5 million pounds per year are imported into the U.S.

Montan waxes are produced primarily in Germany by Hoechst. The U.S. produces about half of its consumption of 5 million pounds per year. The single U.S. producer is American Lignite Products Co., Ione, California. The remainder has been imported from Germany. With the fall of the "Iron Curtain" and the reunification of Germany, increased supplies are expected from the very large mine in former East Germany. In addition to Hoechst, Strohmeyer and Arpe import a montan wax originating from the same mine in East Germany. China, USSR and Czech Republic are also known to have deposits of montan waxes.

Table 7 shows the estimated consumption and imports of natural waxes into the United States.

TABLE 7. NATURAL WAXES - U.S. IMPORTS AND CONSUMPTION

Product	U.S. Consumption (est.) (million lbs/yr)	1991 U.S. Imports Volume (million lbs/yr)	Value (per lb.)
Beeswax	10	1.8	$1.34
Carnauba Wax	6.7	6.7	$1.67
Candelilla Wax	0.5	0.5	$1.15
Montan Waxes	4-5	2.2	$0.82

(3) Prices of Natural Waxes

It is not always easy to compare the relative prices of waxes. A good starting place is the weekly price listing of chemical and related products in the *Chemical Marketing Reporter*, as shown in Table 8 (Reference 39). However, contract prices are often lower. Special grades of higher purity, better color or with FDA approval may be substantially more costly. (Cf. Tables 5 and 6.) Even though import prices are accurate, varying conditions of each transaction can make this source very misleading.

TABLE 8. PRICES OF NATURAL WAXES

Beeswax, bleached, slabs, 100 lb/carton	$2.75/lb
Carnauba Wax, #1 yellow, bags, ton lots	$3.25/lb
#2, centrifuged, ton lots	$1.10/lb
Candelilla Wax, refined, bags	$2.50/lb
Montan Wax, crude, German import	$0.575/lb
California pure, bags	$0.61/lb
Ouricury Wax, refined, pure, bags	$3.25/lb
Japan Wax, case	$7.50/lb

5. SYNTHETIC WAXES

a. Introduction

One of the goals of this program is to find synthetic waxes to replace microcrystalline petroleum waxes that qualify under MIL-W-20553D for desensitizing waxes. Selection of a synthetic material could eliminate many of the current problems with these waxes. The use of uniform feedstocks would eliminate the inherent variations in composition of crude oils. Continuity of supplies would be improved and would not be production limited by petroleum refiners. Changes in chemical structure could be made readily to achieve desired changes in melting point, molecular weight, viscosity or other properties. Potentially the U.S. chemical industry could tailor-make waxes to meet all specifications in adequate volumes of uniform quality. Information was collected on several promising candidates, some already in commercial production.

The search focused on finding materials that would be in the range of MIL-W-20553D specifications. However, each class of material would have to be evaluated. It is quite possible that waxes melting above 200°F would be useful. The test for oil content, which was designed for petroleum products, may give erroneous results for synthetic polymers. Better compatibility with TNT, RDX or other explosives might be more important than other physical properties.

Although it would be most desirable to have new materials meet existing specifications, it may be necessary to make changes. New analytical tests are being used to analyze waxes, and it may be useful to use them in specifying a new wax; e.g., DSC (Differential Scanning Calorimetry) and GC (Gas Chromatography). Suppliers have been asked to provide such data.

The following sections discuss each class of synthetic wax that should be evaluated. Products often are available from several suppliers. Whenever possible, specific commercial products are identified to use as a starting point for testing, but it must be recognized that modifications may be necessary. Selection of candidates is primarily on a technical basis. However, price and location of production plants are discussed because these are so important to procurement of U.S. military supplies.

b. Low Molecular Weight Polyethylene Waxes

Low molecular weight (<10,000) polyethylenes having wax-like properties are produced commercially. They are used mostly in blends with petroleum waxes. The large capital cost has limited the number of production plants. The U.S. market for polyethylene waxes is estimated at 150-170 million pounds per year. This includes homopolymers (30%), oxidized low and high density polyethylenes (50%), and copolymers (15%).

The leading U.S. suppliers are Allied Signal (50%), Eastman Chemical (25%), Hoechst Celanese (15%) and Petrolite. Marcus Oil and Chemical and BASF entered the market in 1989 and early 1991, respectively. Polyethylene waxes are made either by high pressure polymerization, low pressure polymerization with a Ziegler catalyst, or controlled thermal degradation of high molecular weight polyethylene. Polyethylene waxes are available in bulk molten form and in the solid form: diced, prilled, powdered and micronized.

Polyethylene waxes also may be modified by reaction with polycarboxylic acids, such as maleic at elevated temperatures. The resulting acidic polymers can then be further modified to form esters, etc. These should also be considered for testing as desensitizing waxes.

The general class of polyethylene waxes is very promising for the following reasons:

- There are several existing U.S. producers.
- The technology is well known and a proven commercial success.
- While there are some process differences among the producers, it is likely that more than one company would be able to produce a special desensitizing wax.
- A wide range of molecular weights can be made.
- Prices are higher than for microcrystalline waxes, but not unreasonable and advantages could easily be worth the added cost.
- The processes can make straight chain paraffin types of waxes or produce branched chain isoparaffins resembling microcrystalline waxes.
- The branched chains can be controlled by modification with a copolymer, e.g., propylene, butylenes, hexenes, etc.

Allied Signal pioneered the production of low molecular weight polyethylene waxes. They still have 50% of the market and a wealth of experience in making products to meet specific end use requirements. They have one product, AC-656, an oxidized homopolymer, approved for military use in pressed explosives. It is suspected, but Allied would not confirm, that AC-617 is used as the starting polymer for AC-656. They have a very broad product line including homopolymers, oxidized homopolymers, high density oxidized homopolymers and copolymers with acrylic acid or vinyl acetate. However, they do not make copolymers with propylene, butylene or higher olefins.

Eastman Chemical also has a broad line of low molecular weight polyethylenes marketed as Epolenes. The E series are emulsifiable and the N series are non-emulsifiable. It is reported that their process produces somewhat higher molecular weight materials than Allied's. The Epolene N series appears to have potential candidates.

Hoechst Celanese also includes low molecular weight polyethylene waxes in their very extensive line of waxes, many of which are imported from Germany. Polyethylene wax PE 130 has a molecular weight of about 3000 daltons, melts at 125°C by ASTM D-566, and has an acid number of 0.

Petrolite manufactures their own polyethylene waxes. They claim (and it has been confirmed by competitors) to have a wide range of molecular weights from 400 to 3,000. The waxes contain practically no side chains (i.e., they are normal paraffins). If branching is needed, they also make a line of copolymers with propylene, butylenes and hexene. They believe they can make a synthetic wax that could replace microcrystalline petroleum wax in explosives.

TABLE 9. LOW MOLECULAR WEIGHT POLYETHYLENE WAX CANDIDATES

Product	Melting Point (ASTM #)	Price (Bulk, liquid, plant)
Allied-Signal		
AC-617 (homopolymer)	96.5°C (D-127)	\$1.20/lb
AC-656 (oxidized homopolymer)	96.5°C (D-127)	\$1.28/lb
AC-400 (copolymer-vinyl acetate)	90.5°C (D-127)	\$1.28/lb
Eastman Chemical		
Epolene N-14 (homopolymer)	106.3°C (Ring & Ball)	\$1.20/lb
Petrolite		
Polywax 500 (homopolymer)	89°C (D-127)	\$1.09/lb
Polywax 655 (homopolymer)	99.6°C (D-127)	\$1.09/lb
Petrolite CP-7 (copolymer)	95°C (D-127)	\$1.08/lb
Hoechst Celanese		
Hoechst Wax PE 130 (homopolymer)	122°C (D-566)	N/A

c. Alpha Olefin Residues

There are three major producers of α-olefins in the United States today. Each employs a similar process for the oligomerization of ethylene using a triethylaluminum catalyst (or similar one) at 130-250 atm and 150-200°C. Normally, even numbered carbon atom linear alkenes are made from 1-butene to 30+ carbon atoms. The double bond is at the end of the chain. The process also yields a C_{30+} residue which is approximately 10% of the total output. It is disposed of in fuel or fed to crackers, but usually never nets more than 30 cents per pound.

Following are the three producers with their size and location of plants:

Chevron Chemical	500 million pounds	Cedar Bayou, Texas
Ethyl Corp.	1,000 million pounds	Pasadena, Texas
Shell Oil Co.	1,235 million pounds	Geismar, Louisiana

Chevron is the only one that markets a C_{30+} α-olefin fraction. However, they now have a project for a so-called "2 stage residue" product from the C_{30+} fraction. A final decision will be made in three-four months. A price has not been set for the new fraction, but it should be in the same range as other α-olefins; i.e., around 60 cents per pound. Chevron provided the following data as well as DSC and gc curves:

	"2 Stage Residue"	C_{30} Feed
mp (D-127)	82 °C	71 °C
Viscosity at 100°C (D-445)	12.2	8.0
Color Saybolt	+12	+12

Chevron also commented by letter, September 3, 1992, on their ability to meet requirements of MIL-W-40553D as follows:

> "Recalling our recent telephone conversation, the drop melt point and oil content of the wax were of great interest to you. Adjustment of our process variables would allow us to produce a wax in the 85-90°C range; however, meeting a 2% oil content specification presents difficulties. If your concern is strictly the amount of low molecular weight material in the wax, we are confident that this is well below 1%, however, our wax will not meet a 2% specification based on the ASTM method for oil content. The method calls for the sample to be heated in solvent, cooled and filtered. After removal of solvent from the filtrate, the material that remains is considered to be the oil. In our case, the material that remains is a solid that has a molecular weight profile similar to the bulk wax sample. We therefore believe that the high "oil content" arises from increased solubility of our wax relative to paraffinic wax."

Alpha olefins should be evaluated in two ways: (a) the Chevron "C_{30+}" and "2 Stage Residue" should be considered as desensitizing waxes and (b) PAO (poly α-olefin) products can be prepared by dimerizing, trimerizing or polymerizing individual α-olefins or mixtures thereof into higher molecular weight hydrocarbon oils and waxes. Ethyl is very active in this field. Mobil 1 synthetic engine lubricant is one example of a PAO.

d. Ethylene-Methyl Acrylate Copolymers

Chevron Chemical Co. manufactures a line of ethylene-methyl acrylate copolymers. The concentration of methyl acrylate ranges from 2% to 32%, with most grades between 18% and 24%. The polymers are less crystalline and softer than polyethylene. Typical melting points are 76-83°C, as determined by DSC. They have excellent heat stability and low volatiles when processed at high temperatures. Their melt flow index (ASTM-1238) at 190°C and 2.18 kg weight range from 2 to 100 grams per ten minutes.

It is recommended these be looked at as desensitizing waxes. Sixteen different grades are available. Following are three specific grades:

TABLE 10. CHEVRON EMAC RESINS

	SP2220	SP2260	SP2205	DS1278
Methyl Acrylate %	20	24	20	20
Melt Flow, g/10 min	20	2	2	100
Melting Point (by DSC)	83°C	76°C	83°C	N/A
Price, truck load, ¢/lb	91	95	88	93

A somewhat similar type of polymer was mentioned above in the section on low molecular weight polyethylenes - Allied Signal's ethylene-vinyl acetate copolymers. The two should be compared with each other. The Chevron EMAC resins are substantially less expensive than Allied's polyethylene-vinyl acetate copolymer.

e. Polypropylene Homopolymers and Copolymers

Amorphous polypropylene (APP) was a by-product of early polypropylene production. Currently, new processes have reduced the yield of APP to nearly zero. However, to satisfy the demand for APP that had developed as a wax additive, Eastman Chemical has built a specific new plant to make APP and copolymers. These are marketed under the trade name Eastoflex. Five classes of products are made: (1) homopolymers, (2) propylene-ethylene copolymers, (3) propylene-butene copolymers, (4) propylene-hexene copolymers and (5) ethylene-propylene-butene terpolymers. In addition to commercial items, a broad line of new developmental polymers is now offered. Excellent heat stability and compatibility with numerous polymers are claimed.

Another polypropylene homopolymer, Epolene N-15, is included in Eastman's line of low molecular weight polyolefins. However, the melting point of Epolene N-15 is 163°C (325°F), which probably is too high for a desensitizing wax.

This series of new products is certainly a candidate for the R&D program. The products with the lowest melting ranges (by ring and ball method) would be a good starting point.

TABLE 11. EASTMANS'S NEW EASTOFLEX PRODUCTS

Name	mp		Price, ¢/lb (Truck load)
Eastoflex 1010 Propylene homopolymer	150°C	302°F	68
Eastoflex D125 Propylene-butene copolymer	80°C	176°F	91

TABLE 11 (continued)

Eastoflex D-147 Ethylene-propylene-butene terpolymer	85°C	185°F	89

f. Montan Waxes

Montan waxes are obtained by the solvent extraction of lignite. A huge mine in Amsdorf, Germany (formerly East Germany) supplies about 85% of the world's production. Hoechst purifies the waxes in Germany and markets them in the U.S. through Hoechst Celanese. Strohmeyer and Arpe also import a cruder montan wax, also from the Amsdorf mine. American Lignite produces waxes from a lignite deposit at Ione, California.

Montan waxes vary depending upon the lignite from which they are recovered. Extracted material runs about 80% wax and 20% resin and asphalt. The wax component is in the range of 65% long chain C_{24}–C_{36} esters, 25% long chain acids and 10% long chain alcohols, ketones, and hydrocarbons. The resin portion contains terpenes and resinic acids, while the asphalt is believed to be polymerized esters of oxy resinic acid.

American Lignite Products Co. is the only U.S. producer. Their capacity is 5 million pounds per year with production around 3 million pounds per year. They claim to have lignite reserves of 200 million tons which contain 20% wax or enough to last for many years. Their ALPCO waxes are available in seven grades. The largest use is for one-time hot-melt carbon paper inks. Montan waxes are also chemically modified for many end-uses. The following waxes are available as stock items:

TABLE 12. MONTAN WAXES FROM AMERICAN LIGNITE PRODUCTS

	Melting Point (ASTM F-766)		Acid Value (ASTM D-1386)	Price ¢/lb. (Truck load)
ALPCO 16	178-185°F	81-85°C	30-50	63.5
ALPCO 1650	179-186°F	81.5-85.5°C	12-20	64.5

Hoechst Celanese imports montan waxes from Germany. For approximately 70 years these have been purified by batch process at Gerstofen, Germany. The crude wax is subjected to chromic acid oxidation, which attacks the tertiary substituted carbon atoms as well as the dark components, leaving only the linear alkyl portion of the wax intact. A major component is montanic acid or octacosanoic acid – a C_{28} straight chain linear alkyl acid. Hoechst Wax S has a typical chain distribution between C_{24} and C_{36}. They claim their montan waxes are much purer than those from either American Lignite or Strohmeyer and Arpe. A thorough discussion of this technology is presented by A. J. Warth in his book on waxes (Reference 1).

Hoechst Celanese advises that the best product for a desensitizing wax is a 50-50 mixture of Hoechst Wax S and KP (or KPS). This is essentially the same formula developed by Germany for use in World War II, but the report is not available. They also state that this formulation is supplied to NATO forces. This claim has been verified by other sources.

TABLE 13. MONTAN WAXES FROM HOECHST CELANESE

	Drop Point (ASTM D-566)	Acid Number (ASTM D-1386)	Price (Truck load)
Hoechst Wax S	84°C	140	$2.44/lb.
Hoechst Wax KP*	85°C	25	$2.24/lb.
Hoechst WAX KPS	82°C	35	$2.25/lb.

* Not kept in stock; 8 weeks needed for delivery.

From a technical viewpoint, the mixture of Hoechst Waxes S/KP obviously works for NATO although it was not disclosed whether for cast or pressed explosives. From their list of products, Hoechst Wax KP302, with mp of 89°C, and acid number of 21 and Hoechst Wax O, with mp of 120°C and acid number 12, might also be interesting for cast explosives.

A foreign source for a key military ingredient is obviously a problem. However, if an ideal wax based on montan wax can be found, perhaps American Lignite could gear-up to produce an equivalent product domestically.

g. Fischer-Tropsch Waxes

Polymethylene wax is produced in the Fischer-Tropsch process by polymerizing carbon monoxide in the presence of hydrogen at high pressures over an iron catalyst. The products have primarily straight chains with little or no branching. Soft and hard waxes can be made with melting points from 45°C to well over 100°C. Moore and Munger are exclusive importers for the SASOL materials from South Africa (based on synthesis gas from coal). The basic wax is Paraflint H1 while C1 and C2 are derived from H1 but with higher and lower melting points. Oxidized waxes are also available with congealing points of 174°F-260°F and acid number of 10-38.

TABLE 14. FISCHER-TROPSCH WAXES

	Congealing Point (ASTM D-938)		Acid Number	Price ¢/lb. (Truck load)
Paraflint H1	208°F	97.8°C	-	69
Paraflint C1	192°F	88.9°C	-	62
Paraflint C2	221°F	105.0°C	-	99
Paraflint A3	260°F	127.0°C	10	82
Paraflint A6	174°F	97.0°C	38	85

Shell Oil Co. recently announced a new 500,000 metric ton per year middle distillates plant in Malaysia based on synthesis gas using a Fischer-Tropsch process. In addition to middle distillates, Shell will produce a full range of F-T waxes for export to Shell in the U.S. by 1993. It is thought the crude wax will be refined in the United States. Samples are available only on a very limited basis and prices have not been established.

Technically, F-T waxes could extend the melting point ranges of microcrystalline waxes and perform in much the same manner. F-T waxes have never been seriously considered for desensitizing waxes because of their exclusively South African source. However, now that Shell plans to dedicate a full sized plant to F-T waxes, the Shell products should be considered. If the final purification and marketing are done in the U.S., it would be similar to the situation in which microcrystalline waxes are recovered in the U.S. from imported crude oil.

h. Hydrocarbon Resins

This group of resins contains a large variety of polymers with molecular weights around 2000. The raw materials are coal tar fractions for coumarone-indene resins, cracked petroleum residues for aliphatic and aromatic resins and turpentine for terpene resins (i.e. polymerized ß-pinene). The most important commercial products today are the resins from petroleum such as dicyclopentadiene-based resins and those containing aromatics. It would be impossible to outline all the various commercial resins with their many types of modifications. A number are prepared by the condensation of monomers like coumarone and indene or ß-pinene with Friedel-Craft type of catalysts (e.g. $AlCl_3$, BF_3, $SbCl_5$, H_2SO_4, etc.), hydrogenation to remove unsaturation, and reaction with maleic anhydride to give acidic groups.

The commercial use of these "hydrocarbon resins" has grown very little in recent years. The products are often dark in color and variable in quality. However, their raw materials are available at low cost and the industry continues to upgrade them in efforts to increase their value.

Many of these resins are compatible with waxes and polymers used as synthetic waxes. Some of those with melting points in the 80-100°C range should be looked at in desensitizing waxes.

Neville Chemical Co. offers a broad range of these resins. Following are a few examples of specific resins taken from each category as a starting point. In most instances, a similar competing material is also available from other producers.

TABLE 15. NEVILLE CHEMICAL CO. HYDROCARBON RESINS

Type of Resin	Softening Point (ASTM E-28)	Price ¢/lb (Truck load)
Coumarone - indene		
CUMAR R-13	100-110°C	75
CUMAR R-17	67- 85°C	71
Hydrocarbon - alkylated		
NEUCHEM 70	69- 75°C	78
NEUCHEM 100	98-108°C	72
Hydrocarbon - aliphatic		
NEUTAC-80	80- 85°C	73.5
SUPER NEUTAC-99	95-104°C	73.5

Hercules Eastotac products are hydrogenated C_5 aliphatic hydrocarbon tackifying resins. They are made from petroleum feedstock by polymerization followed by hydrogenation. The desired softening point of these fully saturated resins is obtained by controlling the polymerization. As a result, they have good color and heat stability with broad compatibility with other resins. The lowest melting resins offered are the Eastotac H-100 series with a ring and ball softening point of 100°C. Prices vary from 93 cents per pound for Gardner Color <1 to 63 cents per pound for Gardner Color 8 (truck load).

TABLE 16. SUPPLIERS OF HYDROCARBON RESINS

Exxon Chemical Co.
Chemfax, Inc.
Goodyear Tire and Rubber Co.
Hercules, Inc.

TABLE 16 (continued)

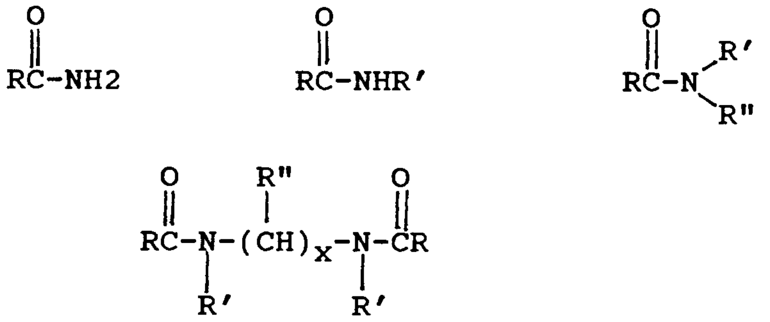
Arizona Chemical Co.
Lawter International, Inc.
Witco Corp.
Resinall Corp.
Sartomer Co., Inc.

i. Amides

Amides derived from saturated or unsaturated fatty acids have properties that make them attractive to evaluate as desensitizing waxes. They are neutral and relatively high melting solids. The low reactivity of amides make them desirable for uses where harsh conditions exist, such as high temperature, pressure and shear.

One can tailor-make amides by varying the R groups. Primary amides are made with a fatty long-chain alkyl or alkenyl acid of C_5-C_{23}. The substituted amides contain a fatty chain R but the R′ and R" substituents may be H, alkyl or alkenyl groups. Further modifications are possible where one or both of the R′ and R" groups are alkylene oxide condensation groups.

TABLE 17. STRUCTURES OF COMMERCIALLY AVAILABLE AMIDES



$$R\overset{\overset{O}{\|}}{C}-NH2 \qquad R\overset{\overset{O}{\|}}{C}-NHR' \qquad R\overset{\overset{O}{\|}}{C}-N(R')(R'')$$

$$R\overset{\overset{O}{\|}}{C}-\underset{\underset{R'}{|}}{N}-(\overset{\overset{R''}{|}}{CH})_x-\underset{\underset{R'}{|}}{N}-\overset{\overset{O}{\|}}{C}R$$

By proper selection of the R, R′ and R" groups, the melting point can be varied and many other properties such as viscosity, penetration or compatibility with polymers and waxes can be adjusted.

Using only commercially available fatty acids, and primary or secondary amines, a very large number of variations can be made. The existing manufacturing plants could most likely be used to produce new amines that are not now commercial products. In fact, the major manufacturers like Akzo, Humko and Sherex are anxious to work on new products. Many different products could be made given the demand.

It was learned by private communication with the Chem Cor Co. that they had spent 1-1/2 years working with Picatinny Arsenal on development of synthetic waxes (including low molecular weight polyethylenes) for emulsion systems. They found several amides that seemed promising but ran into problems on stability tests. The problem seemed to arise from traces of amines remaining in the amides. The important conclusion is that amides can function as wax desensitizers. The problems experienced might not be the same for non-aqueous systems or could be overcome with proper purification or inhibitors.

Several amides with melting points in the range of 85-95° are listed below. Some melting slightly outside this range are also given for comparative purposes. All of them have been commercial products. Often, blends can be made to achieve specific properties.

TABLE 18. COMMERCIAL AMIDES FOR WAX SUBSTITUTES

Product	mp	Price
Stearamide	98-108°C	$1.36/lb
Armid 18 - Akzo Kenamid S - Humko Adogen 42 - Sherex		
Erucamide Armid E - Akzo Kenamid E - Humko Adogen 58 - Sherex	75-86°C	$2.56/lb
Stearyl Stearamide Kenamid S-180 - Humko	92-95°C	N/A
Coco Fatty Amide Armid C - Akzo Adogen 60 - Sherex	85°C	$1.58/lb
Oleamide Kenamid U - Humko	68-78°C	$1.30/lb
Erucyl Stearamide Kenamid S-221 - Humko	80-82°C	N/A
Stearanilide Emery A-805R (now Henkel)	80-82°C	N/A

j. Alcohols, Esters And Ketones

Naturally occurring fats and oils yield many acids, alcohols and esters. Ketones are also made from fatty acids. Many of these products are wax-like solids with melting points in the 80-90°C range. Some have already shown promise in explosives, which justifies looking for other candidates to evaluate.

The melting points of fatty alcohols are generally too low to permit use as is in explosives. However, their potential value is as a component in esters with various fatty acids.

Alcohols derived from the alpha-olefins are available in the C_{20}+ range. Ethyl offers a product containing 66% linear and branched alcohols C_{18} through C_{32}. Vista offers an ALFOL 22+ product with 5% C_{20}, 51% C_{22}, 27% C_{24}, 11% C_{26} and 6% C_{28}. The Emery Group of Henkel offers 2-octyldodecanol-1 and Proctor and Gamble sells 1-octadecanol (stearyl alcohol) as well as C_{16}-C_{18} tallow fatty alcohol.

Waxy ketones can be made by the catalytic decarboxylation of the corresponding fatty acid. The ketones generally melt 15-20°C higher. For example, stearic acid, mp 70°C, yields stearone, mp 87-88°C (commercial products have somewhat lower melting points). A. H. Warth (Reference 1) reported that the Germans developed a ketone of 90°C melting point from an oxidized montan wax and a Fischer-Tropsch wax acid for use as a desensitizing compound in the African campaign of WWII.

Kemp and Anthony (Reference 5) in their study on synthesis of new waxes found octadecyl terephthalate, mp 82°C, to be very promising. They also recommended further study of octadecyl stearate, mp 56°C. Included in the study were many esters including aliphatic dicarboxylic esters, bisphenol-A esters, esters from polyols, maleic acid esters, esters from hydroxyethyl terephthalate and aromatic carboxylic esters. A further recommendation was to continue synthesis of aliphatic and aromatic esters. Included in this study were pentaerythritol tetrastearate, octadecyl terephthalate, 12-hydroxy stearic acid, and monostearin.

An in-depth evaluation by Hogge and Cousins (Reference 9) of octadecyl terephthalate and 12-hydroxy stearic acid showed that they did not perform as well as microcrystalline wax and therefore were not recommended for large scale studies.

Calcium stearate, barium stearate and stearic acid are used in explosives today. Zinc stearate is a commercial product and should be evaluated.

k. Carbamates, Imines And Imides

The previously described work on synthetic waxes by Kemp and Anthony (Reference 5) and Hogge and Cousins (Reference 9) also included study of a number of carbamates and imides. Only one, *N*-octadecyl-*O*-docosanyl carbamate, was in the final evaluation, but it did not perform as well as micro-crystalline wax. It was not recommended for further studies. In H-6 it failed to inhibit TNT sublimation. Its crystallization pattern and its subsequent effect on the crystallization of TNT was significantly different from that of microcrystalline wax.

Phthalimides with long-chain alkyl groups have been found to be very wax-like. They are made from phthalic anhydride and an alkyl amine. Pure *N*-octadecyl phthalimide melts at 96.5 °C. Commercial grades would be expected to be somewhat lower melting. Different imines could be made using C_{20}-C_{22} amine, soya amine, tallow amine, hydrogenated tallow amine, etc. Substitutions could also be made on the aromatic ring.

This general class of nitrogen-containing waxes would appear to have a low probability for providing a new wax substitute.

6. STRUCTURE OF THE U.S. WAX INDUSTRY

Petroleum companies continue to dominate the U.S. wax industry because they are the source of the majority of raw materials for waxes. However, with a large share of the market being lost to new polymers as in the replacement of waxed paper by polyethylene in bread wrappers, many oil companies have cut back on direct marketing and technical product service. Some have maintained direct sales to very large customers, while supplying distributors for the many small customers. Some have completely dropped marketing of waxes. Technical service is more and more in the hands of distributors.

In the non-petroleum wax area, distributors and brokers predominate. Some have exclusive arrangements, like Moore and Munger for South Africa Fischer-Tropsch waxes, but most try to offer a complete line of waxes. As newer synthetic products are accepted, the company developing them usually sells direct, e.g., Allied-Signal, Petrolite and Eastman Chemical. Vegetable and animal waxes are normally handled by distributors and brokers. Multi-national companies like Hoechst Celanese both import (montan waxes) and manufacture (polyethylenes) and sell direct.

About 70% of all waxes are sold by manufacturers direct to customers and about 30% through brokers and distributors. The trend is clear that petroleum companies are reducing marketing efforts. Distributors are increasing their efforts to develop new products, and one, IGI Boler, has become a manufacturer.

7. MILITARY MARKETS FOR DESENSITIZING WAXES

To obtain an overall picture as to the military annual requirements for desensitizing waxes, contacts were made with the Rock Island Arsenal, Picatinny Arsenal, Holston Defense Corp., Industrial Raw Materials, Petrolite, and several consultants in this area.

Holston Defense Corp. reports (Reference 10) that approximately 1.5 million pounds of microcrystalline wax was used for Composition B in 1973. This, of course, was resulted from the Vietnam conflict. Reagan rebuilt inventories during the 1980s. The Gulf War depleted inventories again, but these have been rebuilt; so today, inventories are adequate. Apparently there is also an interim hold on any further procurement of Composition B.

Rock Island Arsenal was especially helpful in supplying an overall view. In the U.S. the industrial demand for explosives is approximately ten times larger than the military needs of 4-5 million pounds per year. However, the use of desensitizing waxes is mostly for military applications. If 1% wax were used in all instances, this would mean an annual need for 50,000 pounds of wax. A continuing war could consume many times this amount.

A very important new trend in military explosives could significantly increase the need for better waxes. Adoption of "smart" weapons will decrease the volume of explosives needed but increase their cost. For example, new Composition B explosives cost $8-15 per pound as compared to traditional Composition B at $4-5 per pound.

In this case, a higher cost wax more easily could be justified. The need for reliability is increased. All of this makes a good case for developing a new synthetic wax to eliminate the problems with petroleum waxes.

Composition B (1% wax) appears to be the largest overall consumer of waxes. Composition D-2 is also important – it contains 84% wax, but total wax content of explosives containing D-2 will average 4-5% wax. It has been estimated that it takes 6 million pounds of Composition B to fill the pipe line (inventories, etc.). This means 60,000 pounds of wax for replenishment.

Holston Defense Corp. supplies nearly all of the Composition B and D-2 requirements. They state that their use of waxes for Composition B (1% wax) was 50,000 pounds in 1991, 60,000 pounds in 1992 and 47,000 pounds estimated for 1993. (Comp. B for the Gulf War was taken mainly from inventories.) However, for D-2 their use of waxes was 512,000 pounds in 1991 and 149,000 pounds for one order in April 1992. Industrial Raw Materials Corp. also stated they had shipped Holston about 500,000 pounds of waxes in 1991 for the Gulf War.

During this literature review a QPL was obtained from Picatinny Arsenal for MIL-W-20553D covering desensitizing wax. Unfortunately, it appeared to be out of date (dated February 1983). On this QPL there are two companies qualified: Petrolite with ES-670 and ES-680 and Industrial Raw Materials with Indramic 170-C, 800 and 1670. However, Petrolite says they withdrew their two products in 1990 and no longer supply them. Further, Indramic 1670 is no longer available, so it too must be removed from the list. H.B. Fuller wax HM-2826 has been, or will soon be, added to the QPL. After the literature review was completed, MACH I was able to obtain an updated (7/8/91) QPL for MIL-W-20553 (Table 19). Consistent with the foregoing discussion, the new list contains no Petrolite products but does have H.B. Fuller's HM-2826 wax and Industrial Raw Materials' Indramic 3000 as new listings.

As reported in the section on montan waxes, Hoechst currently supplies desensitizing waxes for NATO. The product, developed during the second World War, is an equal mixture of Hoechst Acid Wax S and Ester Wax KP or KPS. The product costs more than $2 per pound.

Another trend is the move to insensitive explosives that might require different wax formulations. The interest in synthetic waxes is very strong. The use of low molecular weight polyethylene AC-656 in water emulsions has been very successful.

8. FACTORS AFFECTING FUTURE SUPPLY OF WAXES

The future supply of petroleum waxes will be affected by the current trends outlined earlier in 3 a. (4). Decision time is rapidly approaching for many refineries on how to comply with the Clean Air Act Amendments of 1990 provisions. Since gasoline accounts for over 50% of the industry use of crude oil, refining operation will most likely maximize gasoline production. While lubricants (using 1.17% of crude) and waxes (using 0.13% of crude) are still important products, they constitute only a small part of any refinery's output and therefore will be substantially affected by decisions unrelated to wax production or consumption.

Another factor directly affecting the availability of microcrystalline waxes for the QPL list is the potential for change in raw materials. Since crude oils vary in composition, a change in crude supply to a refinery can result in a change of wax composition - great enough to require requalification. The coming refinery shutdowns, changes of ownership and switches in crude oils also could affect qualified products.

TABLE 19. QUALIFIED PRODUCTS LIST FOR MIL-W-20553

QUALIFICATIONS CERTIFIED
JULY 1991

QPL-20553-8
08 July 1991
SUPERSEDING
QPL-20553-7
18 September 1989

FSC 9160

MILITARY QUALIFIED PRODUCTS LIST
OF
PRODUCTS QUALIFIED UNDER MILITARY SPECIFICATION
MIL-W-20553
WAX, DESENSITIZING

This list has been prepared for use by the Government in the procurement of products covered by the subject specification and each listing of a product is not intended to and does not connote endorsement of the product by the Department of Defense. All products listed herein have been qualified under the requirements for the product specified in the latest effective issue of the applicable specification. This list is subject to change without notice: revision or amendment of this will be issued as necessary. The listing of a product does not release the supplier from compliance with the specification requirements.

The Activity responsible for this Qualified Products List is the U.S. Army Armament Research, Development and Engineering Center, ATTN: SMCAR-BAC-S, Picatinny Arsenal, New Jersey, 07806-5000.

GOVERNMENT DESIGNATION	MANUFACTURER'S DESIGNATION	TEST FOR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
	Indramic 1/ 170-C	TT to AMSMU-00-P6 dtd 12/22/72 # 22-1611Z	Industrial Raw Materials Corporation 575 Madison Avenue 4th Floor New York, NY 10022
	Indramic 1/ 3/ 800	MFP Hr J20-2 Ser 0666, 3 Dec 53 TP-2425	Plant: Ter Chemicals, Inc. North Market Street P. O. Drawer P Pass Christian 39571
	Indramic 1/ 1670	MPF Hr J20-2 Ser 0666, 3 Dec 53 TP-2425	
	Indramic 3/ 3000	MPF Hr J20-2 Ser 0666, 3 Dec 53 TP-2425	

Notes: 1/ Qualified for use to make Composition B for Army use.
2/ Qualified for use to make Composition A-3 and Composition A-4 for Army use.
3/ Contact Yorktown Naval Weapons Station (Re: uses)

AMSC/NA
DISTRIBUTION STATEMENT A. Approved for public release: distribution is unlimited.

TABLE 19. (CONTINUED) QUALIFIED PRODUCTS LIST FOR MIL-W-20553

QPL- 20553-8

GOVERNMENT DESIGNATION	MANUFACTURER'S DESIGNATION	TEST FOR QUALIFICATION REFERENCE	MANUFACTURER'S NAME AND ADDRESS
	HM-2828 1/ 2/ 3/ (Formerly WW-0064)	AR-26-86	H. B. Fuller Company 3539 Lexington Avenue N. St. Paul, MN 55126 Plant: H. B. Fuller Company 3500 Executive Boulevard Dallas, Texas 75149

Despite these negative developments, it will still be possible to obtain microcrystalline waxes, but at much higher cost. The large petroleum companies will most likely be unable or unwilling to produce and submit products for qualification. However, a small company, dedicated to produce products to a specific set of specifications and not tied to a specific crude oil, should be able to supply the product. An example is Ter Chemicals Inc., Pass Christian, MS, now listed on the current QPL list of MIL-W-20553D. Even so, the variability of crude oil composition will always give slightly different wax products. It may be necessary to develop tighter specifications.

The future of the entire wax industry is somewhat in doubt, and growth may be very slow. The environmental problems associated with many of the end uses of waxes are very real. The effect of the Clean Air Act on petroleum companies was cited earlier. Solid waste disposal methods will change markets for many wax end uses. Concern for potential health hazards of consumer products as well as for protection of production workers will bring changes. The new trade agreement negotiations, especially those between the U.S., Canada and Mexico, could affect many products.

The development of new products by smaller companies, by wax distributors and also by the larger chemical companies with products replacing petroleum wax will mean further de-emphasis of waxes by oil companies.

All of these changing factors reinforce the advantages to be gained by developing synthetic wax substitutes. Materials based on polymers or chemicals could eliminate dependence on crude oil. One could expect to obtain more uniform products and to be assured continuous supply in time of war, hopefully at reasonable cost.

SECTION III

MECHANISMS FOR DESENSITIZATION OF EXPLOSIVES WITH WAX AND CRITERIA FOR WAX AND WAX SUBSTITUTE SELECTION

1. SUMMARY AND CONCLUSIONS

An important element of the literature search of Task 1 was to review the mechanisms proposed to account for desensitization of explosives by incorporation of wax. This information was used to develop criteria for the selection of waxes and wax substitutes in this program and to support continuing research and development by WL/MNME.

Detonation of a solid explosive is caused by generation and growth of hotspots, which may be created by several general processes including impact, shock, and heating. Specific examples are:

- Adiabatic compression of trapped gas
- Heating by viscoelastic collapse of a cavity
- Friction
- Shear
- Plastic flow

Wax desensitizes by suppressing these processes by:

- Filling voids that otherwise contain gases
- Separating individual crystals of explosive
- Absorbing heat
- Modifying mechanical properties of the explosive
- Reducing friction by lubrication

The following criteria were developed for candidate selection of potentially improved desensitizers:

- Miscibility with molten TNT
- Wetting of explosive crystals
- Melting range generally below 98°C
- Chemical compatibility with the explosive
- Viscosity below 10,000 cP at melt temperature
- High enthalpy (high specific heat and high heat of fusion or transition)
- Moderate strength and modulus
- Reproducible properties
- Assured availability
- Low cost

Substitutes more polar than microcrystalline petroleum waxes and synthetic polyethylene waxes are needed to increase solubility in molten TNT and better wetting of explosive crystals. The Hildebrand solubility parameter (discussed in Section V) offers a useful guide for selecting candidate substitutes. Combinations of additives may be advantageous.

2. DISCUSSION

a. Mechanisms for Desensitization of Explosives With Wax

Any of a variety of stimuli may initiate detonation of an explosive, e.g., shock, impact, friction, and heat. However, in every case the root cause is believed to be the generation of hot spots followed by their growth to generate a self-sustaining detonation wave. Desensitization is achieved by increasing the energy required to create hot spots of critical size, by draining thermal energy from nascent hot spots, and by isolating hot spots so that they will lose too much energy to their surroundings to continue growing and coalescing to become self-propagating.

Likely stimuli for initiation vary depending on the application of the explosive. For example, the shock imparted to a projectile during launch from a cannon is intense, but usually of much shorter duration than the shock imparted to an impacting bomb. Therefore, a desensitizer has less time to operate in the former case. However, in any application the explosive must be insensitive to any stimuli generated during handling, shipping, storage as well as certain nearby explosions, whether due to hostile activity or accident.

On-going research concerning the mechanisms and technology of desensitization can be expected to increase understanding and yield improved control.

TNT and explosives prepared from TNT (such as Composition B and HBX-1) are porous structures. As TNT solidifies from a melt, microvoids are formed. The difference in density of the solid (1.65 g/cm^3) and liquid melt (1.54 g/cm^3) results in shrinkage and the consequent formation of voids and cracks. The coarser the crystals that form, the greater the volume of the voids and the lower the density of the finished explosive (Reference 11). In casting shells containing TNT, the casting solidifies from the outside inward thereby producing a cavity at the center of the casting.

These defects increase the sensitivity of the explosive by allowing the formation of hotspots from:

- Adiabatic compression of gases trapped in the voids and cracks when the explosive is impacted or compressed (Reference 12)
- Viscoelastic work resulting from the collapse of a cavity (Reference 13)

Hotspots may also form during impact or shock by:

- Friction between impacting surfaces and/or grit and grains of the explosive (Reference 14)

- Localized adiabatic shear of the material during deformation (Reference 13)

- Plastic bulk flow of the material, which can trap gases leading to adiabatic compression or can result in viscous heating of the explosive (Reference 14)

The following processes have been suggested to explain the desensitization of Composition B and TNT by waxes:

- Filling some of the microvoids in the porous TNT, thus reducing the population of hotspots from adiabatic compression

- Coating the individual crystals of explosive, thus physically separating hotspots and preventing their coalescence and growth to an explosion

- Quenching of the hotspot by absorbing heat energy

- Alteration of the mechanical properties of the explosive to distribute impact energy over a larger volume

- Lubrication, which decreases generation of heat by friction

The foregoing proposed mechanisms of desensitization are supported by experimental evidence. For example, shock sensitivity has been shown directly related to the pore volume (density) of an explosive (Figure 2).

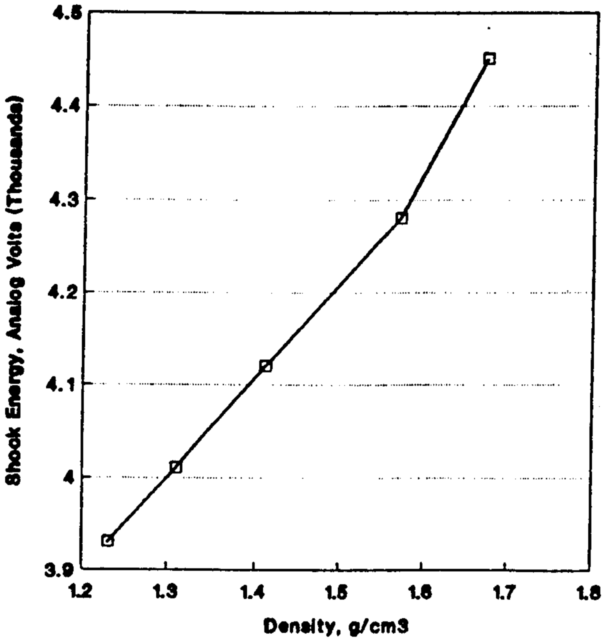


Figure 2. Shock Sensitivity Versus Density Of Explosive

Miscible additives such as chlorowaxes have been shown to reduce pore volume and shock sensitivity (Figure 3) (Reference 15).

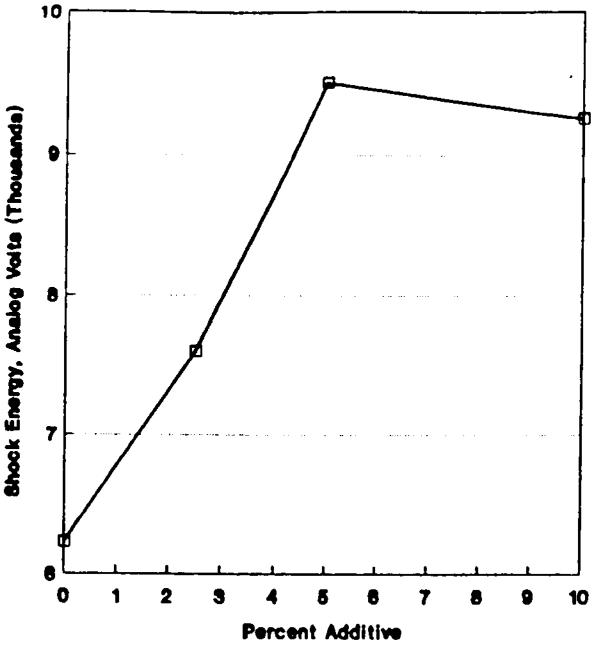


Figure 3. Shock Sensitivity Versus Percent Chlorowax Additive

Wax is homogeneously distributed in TNT to a concentration of about 0.7%. The rest of the wax forms "blebs" in the composition (Reference 11). Thus some microvoids in Composition B or cast TNT are likely filled with wax, which eliminates these sites as initiators for hotspot formation.

Physical separation of hotspots, which inhibits their coalescence and growth, is also implied by experimental evidence. Impact sensitivity has been shown to be inversely related to coating efficiency of desensitizers on RDX (Figure 4).

Well-coated RDX particles exhibit much lower card gap sensitivity than incompletely coated particles (Reference 16).

The mechanism of desensitization by heat absorption is supported by the observation of an inverse relationship of impact sensitivity to the specific heat of a wide range of additives (Figure 5) (Reference 17).

The bullet impact sensitivity of explosives has been related to the enthalpy of a variety of wax desensitizers (Figure 6) (Reference 18).

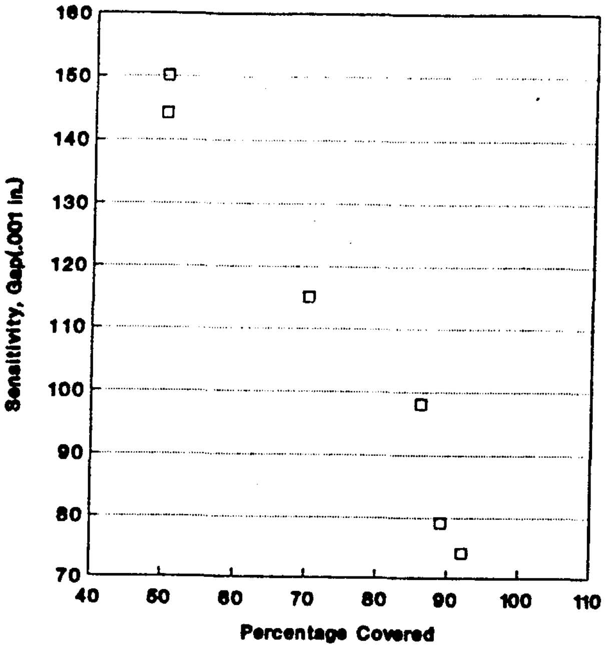


Figure 4. The Effect Of Coating Efficiency on Shock Sensitivity Of RDX

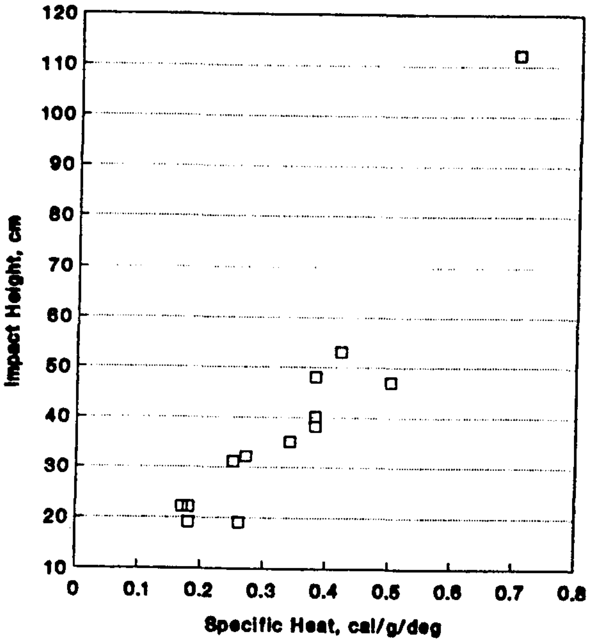


Figure 5. Effect of the Specific Heat Of Additives on Impact Sensitivity

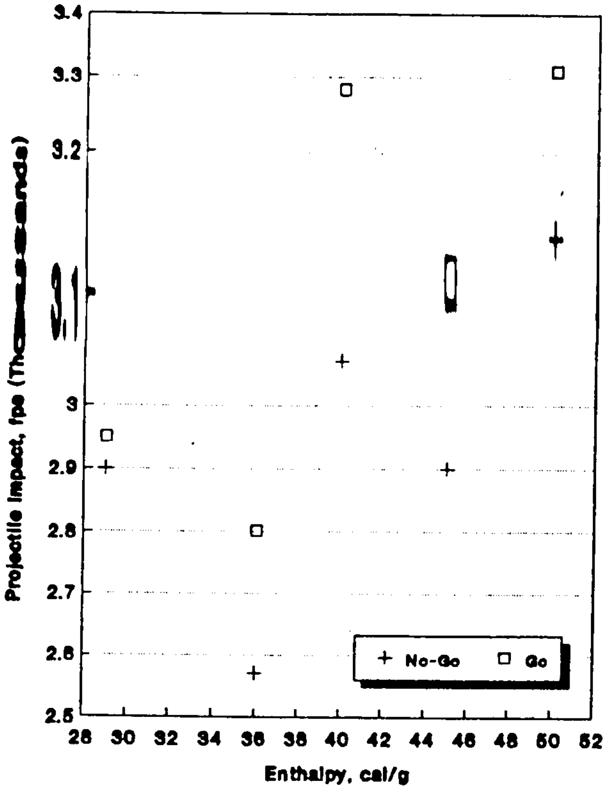


Figure 6. Bullet Impact Sensitivity Versus the Enthalpy Of Wax Desensitizers

Mechanical properties of the additive and the resulting composition directly affect the impact sensitivity of the explosive. Brittle, high-strength polymers sensitize explosives to impact by forming hotspots at crack tips during catastrophic failure during fracture or shear. Lower-modulus polymers spread radially during impact and thus do not cause this problem (Reference 14). Wax, a brittle but low-strength additive reduces the overall tensile and compressive strength of Composition B and TNT (Reference 19), thus lessening the probability of this type of hotspot formation. Recent research on cavity collapse under launch conditions suggests that softened material may collapse slowly during the early portion of the launch, thereby preventing ignition which can lead to in-bore explosion (Reference 20).

Frictional heating has been related to the mechanical properties and thermal properties of the additive. Those additives having high strength, low specific heat, and low heat of fusion cause increased heating (Reference 21). Waxes that desensitize generally have low strength, high specific heat, and high heat of fusion.

b. Criteria For Additive Selection

Additives to replace waxes as desensitizers in explosives such as Composition B and HBX-1 must have many of the desirable properties of waxes but should be free of the shortcomings that gave rise to the present program.

(1) Miscibility with TNT

An additive that is miscible or readily dispersed in molten TNT will probably fill the microvoids in cast TNT. Thus an additive having a Hildebrand solubility parameter closer to that of TNT [estimated 11.6 $(\mathrm{cal/cm^3})^{.5}$] than that of wax [estimated 8.3 $(\mathrm{cal/cm^3})^{.5}$] may provide improvement if the degree of hydrogen bonding is similar (low). (The Hildebrand solubility parameter is defined in Section V).

(2) Wetting of RDX or Other Energetic Components.

Again the Hildebrand solubility parameter of the selected additive may provide guidance for selection of desensitizers superior to wax. RDX [solubility parameter estimated 15.9 $(\mathrm{cal/cm^3})^{.5}$] is clumped in cast Composition B (Reference 11). Better wetting of the RDX by the additive may aid physical separation and thus reduce sensitivity.

(3) Melting Range

To permit current manufacturing procedures to be employed, an insoluble solid additive should melt in the range of 75-98°C. Lower melting ranges lead to exudation (Reference 22) while higher ranges may preclude incorporation into the explosive (Reference 18). However, a higher melting additive may be considered if it is dispersible as a powder or plasticized by an emulsifier or a compatibilizing agent. Compatible, probably more polar, additives may be acceptable even though they melt at temperatures lower than 75°C or are liquids, since exudation will be hindered by the polar attractive forces between explosive and additive. The lower viscosity of such additives may permit faster melt mixing and casting, as well as better wetting, dispersing, and coating of filler – hence better desensitization. Alternatively the low viscosity may allow higher explosive loading.

Suppliers of wax and potential wax substitutes measure melting points or softening points of their products by a variety of methods that give differing results. Several commonly used ASTM methods are described briefly below.

(a) Drop Point Method; ASTM D-127, TAPPI T634

This method generally is used where melting information is needed on wax, such as micro waxes and petrolatums, that exhibit very wide melting range.

(b) Plateau Melting Point; ASTM D-87, TAPPI T630

This method gives the temperature at which most of the given wax changes from a solid to a liquid and is commonly used for paraffin waxes. Some waxes, such as blends or those containing large amounts of non-normal hydrocarbons, may not exhibit a melting plateau.

(c) AMP Melting Point

This is obtained by adding 3° to the ASTM D-87 melting point.

(d) Congealing point; ASTM D-938

This quick and easy procedure requires only a small sample. It is useful to determine the temperature at which a wax ceases to flow. The result is always lower than that determined by ASTM D-127.

(e) Ring and Ball; ASTM D-36, ASTM E-28

This method is used for viscous blends.

(f) Fatty Acid Titer; ASTM D-1982

This method is used to measure the crystallization or solidification temperature of fatty acids.

(g) Vicat Softening Point; ASTM D-1525

This method is used for thermoplastic polymers.

(h) Melting Range MIL-W-20553D

This method is based on differential scanning calorimetry (DSC).

The melting point test for waxes meeting specification MIL-W-20553D is ASTM D-127. The DSC melting range specified as a fingerprint gives more useful information.

Two examples of differences in melting point determined by different methods follow:

1. DuPont reports the softening point of ELVAX 500W by ASTM E-28 as 98°C, and the melting point (by an unspecified method) as 92°C.

2. WL/MNME cites 104°C as the supplier's value for the melting point of Epolene E-14. However, by DSC WL/MNME measured a melting point of 94°C.

(4) Chemical Compatibility with the Explosive

To ensure stability during storage, the additive must not react with the explosive or catalyze its degradation. Most waxes are generally inert and meet this requirement. Substances containing amines or other basic constituents are generally incompatible with nitramines.

(5) Viscosity of the Additive

The viscosity of the additive at the melting range of TNT must be sufficiently low to allow easy incorporation into the TNT. The lower the viscosity of the additive at this temperature, the better. The upper limit of viscosity is about 10,000 cP. However, reasonably high viscosity of the resulting emulsion, can be beneficial by preventing dense components from settling out before the mixture solidifies. This can be important for explosives containing powdered aluminum (Reference 23). Waxes have low viscosities when melted. Blending of additives is one method which can be used to tailor viscosity.

(6) Thermal Properties

Ideally an additive should have high specific heat and either have high heat of fusion or undergo endothermic transitions. These properties favor absorption of heat from nascent hot spots and thereby suppress their growth. The enthalpy of fusion of Indramic wax is reported to be approximately 42 cal/g (Reference 18), and its specific heat is estimated to be 0.4-0.5 cal/g/deg.

(7) Mechanical Properties

The mechanical properties of the additive must favor desensitization of the explosive. High-strength, high-modulus (brittle) additives can sensitize (Reference 14). However, it has been suggested that low-strength, low-modulus (rubbery) additives may promote viscous heating during cavity collapse and thereby sensitize by creation of hotspots (Reference 13). Thus the mechanical properties of the additive should fall between these extremes. Wax is a low-strength, brittle material; replacement by a stronger, but still flexible, substance may provide greater desensitization.

(8) Reproducibility

The chemical and physical properties of the additive must be reproducible – not subject to change as a result of uncontrolled variations in feedstock or processing conditions.

(9) Availability

To be practical, an additive should be readily available without regard to economic, political, or environmental considerations.

(10) Low Cost

Low cost is desirable as long as it does not unfavorably affect availability and performance.

c. Guidance for Present and Future Research and Development

The foregoing considerations suggest the selection of candidate substitutes more polar than microcrystalline petroleum waxes and synthetic polyethylene waxes. This would increase solubility in molten TNT and promote wetting of explosive crystals. The Hildebrand solubility parameter (discussed in Section V) offers a useful guide for selecting such candidate additives.

A combination of two or three substitutes providing differing desensitizing mechanisms might be particularly effective. For instance, a good plasticizer or coupling agent could reduce the viscosity of a stronger plastic so that it could be used, and a fire retardant could quench the heat generation of hot spots.

Explosives may be tailored for differing applications (e.g., shells vs. bombs) by emphasizing on appropriate desensitizing mechanisms.

If a desensitized composition provides inadequate explosive yield or is too insensitive to the fuze, the problem may be solved by choice of a wax substitute that operates by a different desensitizing mechanism.

The wax substitutes offer much greater formulation flexibility than natural or synthetic hydrocarbon waxes. They are synthetic chemicals consistently available in good quantity and quality. Generally they are much easier to emulsify with TNT and NE than microcrystalline petroleum wax. Polywax 600, an unbranched synthetic polyethylene wax is difficult to emulsify with nitroethane (NE), 2,4-dinitrotoluene (2,4-DNT) or TNT because of its lack of branching. The polar wax substitutes are far better choices.

A low-melting or liquid polar wax substitute may be less subject to exudation because of its solubility in TNT or bonding to TNT or explosive fillers. Such additives should reduce viscosity of the melt mix and expedite casting of the product, thereby increasing production rates. Alternatively, more energetic compositions containing higher levels of explosive filler could be processed.

SECTION IV

IDENTIFICATION OF PROCESS AND METHODOLOGY FOR SELECTION OF EXPLOSIVE MATRIX/WAX/EMULSIFIER SYSTEMS

1. SUMMARY AND CONCLUSIONS

The objective of Task 2 is to identify the process and methodology for selection of improved explosive matrix/wax/emulsifier systems for evaluation in both the experimental work of this Phase II program and future R&D to be conducted by WL/MNME.

In a typical melt cast explosive, molten TNT comprises a liquid phase (matrix) in which other ingredients, such as a molten microcrystalline petroleum wax desensitizer and nitrocellulose emulsifier are dispersed. After casting, the mixture is cooled and the resulting solid explosive consists of a coherent mass of TNT crystals coated with desensitizer/emulsifier.

Because the supply and quality of microcrystalline wax are undependable, and because existing desensitizer systems exhibit serious deficiencies, superior replacements are needed. To screen the huge spectrum of potential desensitizers and emulsifiers required development of an efficient, meaningful laboratory procedure using a nonexplosive simulant for TNT.

MACH I developed in conjunction with WL/MNME the following process and methodology.

- Identify the desired explosive matrix.
- Select a candidate desensitizing wax or wax substitute.
- Select a candidate emulsifier. (A single, or combination of, Ganex surfactants proved most promising in the present program.)
- Select an appropriate, nonexplosive simulant for TNT, e.g., nitroethane or 2,4-dinitrotoluene.
- Heat the mixture (explosive simulant/ desensitizer/emulsifier) to the processing temperature (somewhat higher than the melting point of TNT).
- Agitate the hot mixture to form an emulsion. If an emulsion is not formed, the candidate system is rejected.
- Allow the hot emulsion to stand.
- Record the time elapsed until the emulsion breaks (i.e., until phases separate). This is the critical test. Only those systems with emulsion stability of five minutes or more qualify for further evaluation.

After a composition with good emulsion stability is identified by the foregoing procedure, it must be verified by tests in which the simulant is replaced by live explosive. Small scale tests should be conducted to ensure safety and chemical compatibility (e.g., DSC). Following these, the established regimen of acceptance tests should be performed. These include tests for: physical and chemical stability, safety, and performance.

2. DISCUSSION

a. Miscibility (Emulsion Stability) and Homogeneity Test

The emulsion stability test procedure developed during Phase II of this program was based on that used successfully in Phase I. However, in Phase II lecithin was excluded. Therefore, the concentrations of wax and emulsifier were changed slightly to provide the 84/16 wax/emulsifier ratio specified for MIL-C-18164A (OS). Weights of ingredients used in the following procedure are specific for nitroethane as the TNT simulant.

(1) Procedure for Emulsion Stability
(Nitroethane:wax+emulsifier = 3:1)

1. Weigh 1.12 grams of emulsifier into 40 mL vial.
2. Add 5.62 grams of wax to vial.
3. Add 20 mL (21 grams) of nitroethane to the vial, seal, and allow to stand overnight at room temperature in a test tube rack fitted with a handle.
4. Place rack in oven or oil bath at 90-100°C to melt the wax (requires about 1.5 – 2 hours).
5. Shake rack vigorously by hand 10 times (about 5 sec)
6. Allow to stand in the oven or oil bath.
7. Observe at intervals of 0.5, 1, 3, 5, minutes and every 5 minutes thereafter, noting the time at which the emulsion breaks.
8. Measure the depth of the separated top layer.

When 2,4-DNT is used as the TNT simulant, the procedure is similar, but the quantities of reagents used are reduced and the mixture is not allowed to stand overnight.

Several of the variables in the procedure were examined to determine effect on reproducibility. The choice of heating apparatus was determined using Ganex WP-660 emulsifier with Indramic 170C wax and nitroethane simulant. The results shown in the following table indicate that the oil bath gives slightly greater reproducibility.

TABLE 20. EFFECT OF HEATING APPARATUS ON REPRODUCIBILITY OF EMULSION STABILITY

	Emulsion Break Time Oven (min)	Oil Bath (min)
	3	10
	3	30
	10	5
	15	10
	30	10
	30	5
	15	5
Average	15.1	10.7
Standard Error of the Mean	4.3	3.3

The effect of the time in the oven before shaking was set at 90 minutes initially as the time necessary to completely melt the wax. As shown in Table 21, further standing had no discernible effect on the stability times. However, it is always necessary to verify that the wax is completely melted because the rate of melting depends not only on temperature, but also on the melting point and chunk size of the wax.

TABLE 21. EFFECT OF MELTING TIME ON EMULSION STABILITY TIME (1)

Emulsifier	Wax	Emulsion Break 90 min Melting Time (min)	180 min Melting Time (min)
Ganex WP-660	Indramic 170C	10	15
Ganex WP-660	Polywax 600	1	0.5
Ganex V-220	Indramic 170C	10	10
Ganex V-220	Polywax 600	1	1
Ganex 9965-39D(2)	Indramic 170C	45	45
Ganex 9965-39D(2)	Polywax 600	15	15

(1) Nitroethane simulant at 100°C
(2) Experimental product

The effect of variable agitation of the tube containing the mixture was tested by increasing the number of shakes before the emulsion was allowed to stand for observation. As shown in Table 22, a small variation in the shaking does not appreciably affect the emulsion stability. Very large changes in the vigor of the shaking process, however, would be expected to affect the stability of the emulsions.

TABLE 22. EFFECT OF AGITATION ON EMULSION STABILITY TIME (1)

Emulsifier 1	Emulsifier 2	WAX	Emulsion Break 10 Shakes (min)	20 Shakes (min)
Ganex V-216 (30 Wt %)	Ganex WP-660 (70 Wt %)	Polywax 600	3	3
Ganex V-216 (30 Wt %)	Ganex WP-660 (70 Wt %)	Polywax 600	3	3
Ganex WP-660	----	Indramic 170C	3	5

(1) Nitroethane simulant at 100°C.

Temperature is an important variable affecting stability of the emulsion. For example, Polywax 600 does not melt completely until the temperature exceeds 94°C, and an emulsifier will not disperse solid wax. Table 23 shows the result of temperature variation on some emulsion tests using individual and combinations of Ganex emulsifiers. The TNT simulant is nitroethane.

TABLE 23. THE EFFECT OF TEMPERATURE ON EMULSION STABILITY

Emulsifier 1	Emulsifier 2	Wax	Emulsion Break (min) 100°C	95°C	90°C
Ganex WP-660	---	Indramic 170C	10	15	3
Ganex V-220	---	Indramic 170C	10	15	3
Ganex WP-660 (70 Wt %)	Ganex V-216 (30 Wt %)	Indramic 170C	45	30	1
Ganex WP-660	---	Polywax 600	1	3	0.5
Ganex V-220	---	Polywax 600	1	0.5	0.5
Ganex WP-660 (70 Wt %)	Ganex V-216 (30 Wt %)	Polywax 600	0.5	0.5	0.5

Below 95°C the stability appears to decrease, possibly due to the wax not being completely melted. The emulsion tests were generally conducted in the range 95-100°C. The specific temperature is noted for results cited later in this report.

The results of foregoing experiments provided guidance for developing a meaningful and reproducible standard miscibility test.

b. Compatibility Test (WL/MNME)

The compatibility test performed by WL/MNME consists of determining the DSC exotherm temperature of a 1 to 1 mixture of TNT with the experimental sample. Significant depression of the primary exotherm indicates incompatibility. Another sign of incompatibility is a significant increase in the heat released during the primary exotherm. These observations indicate that the TNT is decomposing at a lower temperature or more rapidly as a result of interaction with the added material. Figure 7 shows the raw DSC results of Ganex WP-660 emulsifier with TNT. The maximum of the exotherm was shifted from 303°C for TNT to 275.8 for the mixture. This depression is insufficient to indicate that the emulsifier is incompatible. By way of comparison, the peak exotherm of the explosive formulation made with Composition D-2, Indramic wax with nitrocellulose and lecithin, is reported to be 262°C. Figure 8 shows the DSC record of Solsperse 5000 emulsifier with TNT, where a portion of the exotherm has been depressed to 148°C. This shift is unacceptable.

c. Miscibility (Emulsion Stability, WL/MNME)

This procedure is a modification of the emulsion stability test outlined in MIL-C-18164A paragraph 4.4.5 for Composition D-2 wax. A sample of TNT is placed in a graduated cylinder suspended in a hot bath at 92°C. After the TNT has fully melted, the specified amount of emulsifier is added and the mixture is agitated until all components are melted and thoroughly mixed. The specified amount of wax is then added, melted, and thoroughly mixed. The procedure yields a 3/1 ratio of TNT to wax/emulsifier. Agitation of the mixture is accomplished with a helix-shaped wire. Following agitation the emulsion is allowed to stand undisturbed. The time of initial break of the emulsion is noted as well as the amount of separation as a function of time.

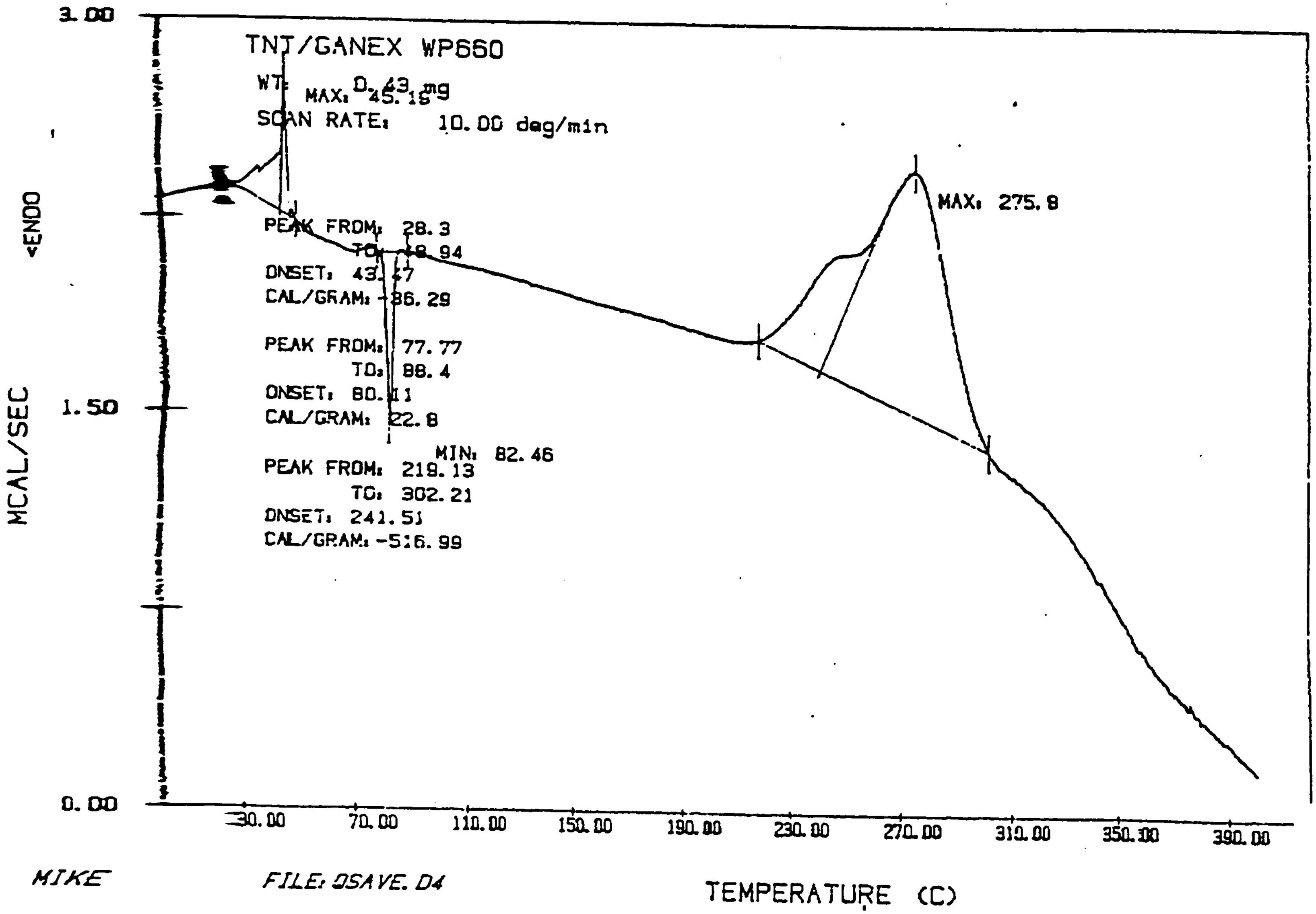


FIGURE 7. DSC Of Ganex WP-660/TNT Mixture

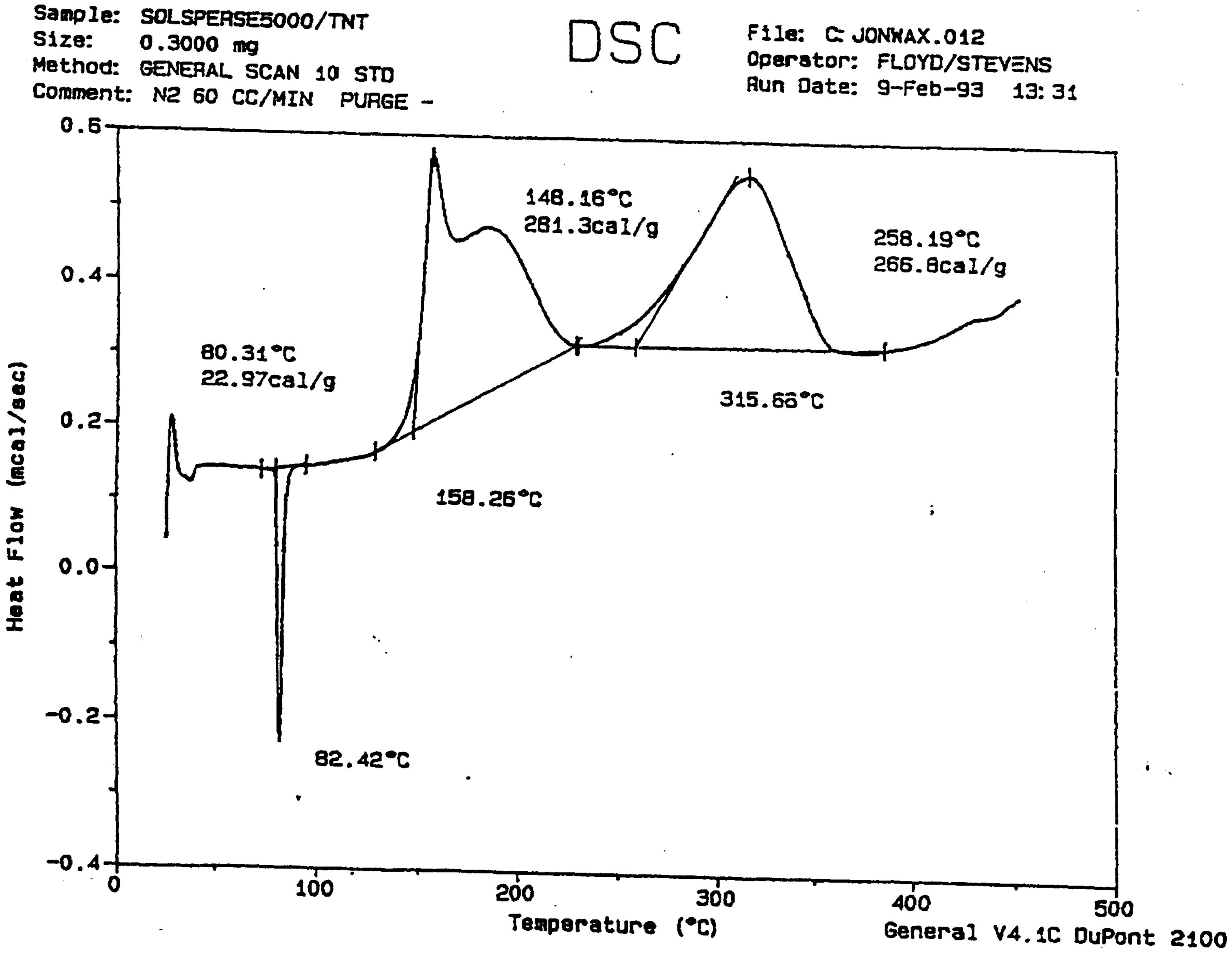


FIGURE 8. DSC Of Solsperse 5000/TNT Mixture

SECTION V

IDENTIFICATION AND SELECTION OF WAXES, WAX SUBSTITUTES AND SURFACTANTS FOR A GIVEN MATRIX (TNT)

1. SUMMARY AND CONCLUSIONS

The objective of Task 3 is to apply the process and methodology developed under Task 2 (Section IV of this report) to selection of improved wax/emulsifier desensitizer systems specifically for melt-cast TNT explosives. For clarity pertinent elements of the general process and methodology are restated here:

- Select a candidate desensitizing wax or wax substitute.
- Select a candidate emulsifier.
- Select an appropriate, nonexplosive simulant for TNT.
- Heat the mixture (explosive simulant/ desensitizer/emulsifier) to the processing temperature (somewhat higher than the melting point of TNT).
- Agitate the hot mixture to form an emulsion. If an emulsion is not formed, the candidate system is rejected.
- Allow the hot emulsion to stand.
- Record the time elapsed until the emulsion breaks (i.e., until phases separate). This is the critical test. Only those systems with emulsion stability of five minutes or more qualify for further evaluation.

This section of the report addresses these elements in greater depth.

To simulate TNT, 2,4-DNT, which melts at 50°C, serves as a more convenient alternative to relatively volatile NE. In most cases the test results with 2,4-DNT and NE agree and correlate well with those obtained using molten TNT. However, in a few instances this is not the case. When possible, it is preferable to use TNT rather than a simulant. Otherwise both simulants should be used, although either one is usually satisfactory.

2. INTRODUCTION

a. Rationale for Selection of a Successful Emulsifier

Selection of a good emulsifier is a complex and difficult process. However, years of experience with a wide range of surfactant applications give valuable insights. Polarity of the surfactant relative to the two liquid phases and the solid particles is critical. The HLB (Hydrophile-lipophile balance) numerical system developed for aqueous emulsions is a very helpful, albeit approximate guide; but it is merely an approximation and is not directly applicable to nonaqueous applications. The Hildebrand solubility parameter for nonaqueous systems is also a helpful guide, but it does not give precise answers. Multifunctional polymeric surfactants often are more effective than monomeric counterparts for dispersing pigments. However, there are no hard and fast guidelines for choice, and no advantage in certain applications. All of these factors were kept in mind while developing emulsifiers for the Phase I and II programs.

Ganex resin surfactants appear to be a unique emulsifiers for wax in NE, 2,4-DNT and molten TNT. Exhaustive testing has not identified a good alternative.

The following rationale guided selection of surfactants that proved to be successful emulsifiers for the three separate systems studied in the present program:

1. Oil in NE at 20°C
2. Oil in NE at 90°C
3. Indramic 170C wax in NE at 90°C

The same approach should be helpful in future surfactant programs. At the outset candidate surfactants were selected from a broad range of surfactants on the basis of outstanding performance in many diverse applications. Thus it is not surprising that a good alternative has not been found for the Ganex family.

Test MIL-C-18164A, Composition D-2, paragraph 2.2.5, was chosen for the evaluation of emulsion stability. Nitroethane was chosen as the simulant for TNT because it has essentially the same nitro-group content as TNT. This was expected to ensure similar compatibility with other components of the formulation.

To ensure that the wax is completely melted, a 90-95°C emulsification temperature is required. Because NE is so volatile at this temperature, it cannot be stirred in an open vial without excessive evaporation. Instead, the vial was capped and agitated by shaking rather than stirring. To develop technique and optimize agitation, initial studies were conducted at 20°C using Sunthene 420 oil in place of wax. Experimental emulsifiers were used at the concentration of nitrocellulose (14%) in Composition D-2. Ten shakes proved to be best for distinguishing between good and poor emulsifiers and was adopted for all subsequent emulsion stability tests.

After tests of only eighteen nonionic, anionic, cationic and polymeric surfactants known to be good emulsifiers in other systems, the four shown in Table 24 were found to provide at least five-minute initial break time, as required by the military specification. All emulsifiers in Tables 24–27 contained 20% of lecithin (Centrol IPUB).

TABLE 24. EMULSION STABILITY OF SUNTHENE OIL AT 20°C

	Initial Break, Minutes
Aerosol OT 100, disodium dioctyl sulfosuccinate	15
Aerosol TR 70, disodium ditridecyl sulfosuccinate	6
Igepon T77, sodium-N-methyl-N-oleoyl taurate	5
PBMA-8.9, polybutadiene/maleic anhydride adduct	12

The sulfosuccinates were selected for evaluation because they have three polar groups favoring physical compatibility with NE and TNT and because they provide particularly small particle size in the emulsion polymerization of certain monomers. The alkyl group length was selected to provide low water solubility, thus favoring physical compatibility with wax.

The taurate was chosen because it has amide and sulfonate groups favoring compatibility with NE and TNT. This product is used as an emulsifier for agricultural herbicides because it wets and adheres to waxy plant leaves, reducing interfacial tension between the herbicide and the leaf to promote rapid assimilation into the leaf.

Polybutadiene/maleic anhydride (PBMA) adduct was chosen because the hydrocarbon polymer backbone is compatible with wax and the repeating maleic anhydride unit along the backbone favors physical compatibility with NE and TNT.

These four emulsifiers and several others were then evaluated at 90°C. Igepon T77 and PBMA-8.9 gave 9 and 10 minute break time, the others were ineffective as shown in the Table 25.

TABLE 25. EMULSION STABILITY OF SUNTHENE OIL AT 90°C

	Initial Break, Minutes
Aerosol OT 100	<1
Aerosol TR 70	<1
Igepon T77	10
PBMA 8.9	9

Sunthene 420 is a naphthenic petroleum process oil (210 Saybolt Universal Seconds viscosity at 100°F) made by Sun Oil Company. It is similar to an SAE 10 motor oil that was shown by Picatinny Arsenal to be a suitable replacement for wax in Composition B. Also, Atlantic Research Corporation used it in developing PBX formulation AFX-931 for WL/MNME.

The four surfactants that were good emulsifiers for Sunthene 420 oil in NE, at either 20°C or 90-95°C, were ineffective with Indramic 170C microcrystalline wax, presumably because the wax is much less polar. The Sunthene oil contains about 35%-40% aromatics, while Indramic 170C is almost entirely paraffinic.

Within the first two months of the program, MACH I:

- Identified a group of alkyl polyvinylpyrrolidone resin surfactants that were excellent emulsifiers,
- Confirmed the test results, and
- Sent samples to WL/MNME to evaluate and verify their effectiveness in emulsifying molten TNT and Indramic 170C wax.

These emulsifiers are made and sold by International Specialty Products Company (formerly GAF) under the trade name Ganex resins (Appendix A).

The alkyl polyvinylpyrrolidone resins family (Ganex surfactants) were selected for initial evaluation because they contain a repeating cyclic amide structure along the polymer chain that favors physical compatibility with NE and TNT (Appendix A). They are used commercially as dispersants in anhydrous cosmetics, which implies compatibility with the wax used in some of these compositions. A review of Ganex resin technical literature then showed that Ganex V-220 is insoluble in nitromethane and nitropropane but partially soluble in NE. It is also soluble in mineral oil. These properties appeared very promising. Structure variations among the three Ganex resin products indicated good flexibility in adjusting for compatibility, emulsion stability, wetting, dispersancy and other required properties.

Although the individual Ganex products were only marginally effective when evaluated in the first group of 20 candidate emulsifiers, they were much better than any of the others. However, with blends of two or three Ganex surfactants emulsion stability increased greatly as shown in Table 26.

TABLE 26. EMULSION STABILITY OF INDRAMIC 170C WAX WITH GANEX SURFACTANT BLENDS AT 90°C

Ganex No.	Initial Break, minutes
V-216	2
V-220	2
WP-660	6.5,4
1/1:216/660	20,10,18,35 (ave 21)
1/1:220/660	18
1/1/1:216/220/660	25
Same, half concentration	20
Same, quarter concentration	7

Igepon T77, which was a good emulsifier for Sunthene 420 oil, greatly improved performance of Ganex WP-660 resin when used as a 1/1 co-emulsifier, even though it was ineffective by itself with Indramic 170C wax. Aerosol TR 70, which could not emulsify either Indramic wax or Sunthene oil at 90-95°C, also greatly improved the performance of Ganex WP-660 resin when used as a 1/1 co-emulsifier. (See Table 27.)

TABLE 27. EMULSION STABILITY OF INDRAMIC 170C WAX WITH EMULSIFIER BLENDS AT 90°C

Ganex No.	Co-Emulsifier	Initial Break, Minutes
WP-660		6.5, 4 (5.3 ave)
WP-660	Aerosol TR70 (1/1)	12, 15 (13.5 ave)
WP-660	Igepon T77 (1/1)	12, 11 (11.5 ave)

All of the foregoing results were obtained with a small amount of lecithin included as a co-emulsifier as specified in the MIL-C-18164A procedure. The lecithin proved to be unnecessary. Depending on the Ganex resin surfactant, emulsion stability was as good or better when no lecithin was present (Table 28). Since the Ganex resin was not increased to compensate for omitting the lecithin, the total emulsifier concentration was reduced by 20%.

TABLE 28. EFFECT OF LECITHIN ON EMULSION STABILITY OF INDRAMIC 170C WAX

Ganex No.	Initial Break, Minutes With Lecithin	 Without Lecithin
V-216	2	8
WP-660	6.5,4	18
1/1:216/220	18	14
1/1/1:216/220/660	25	25

By replacing both nitrocellulose and lecithin Ganex WP-660 resin has eliminated several serious problems attributed to these ingredients. Moreover, this has been achieved using only one-third the former concentration of emulsifier. AFX-644 containing Ganex WP-660 resin is being optimized in its development as a bomb explosive for production.

These results validate MACH I's selection techniques and evaluation procedure using NE simulant for TNT.

b. Polarity of Candidate Systems

(1) Solubility Parameter

At the beginning of this century, J. H. Hildebrand pointed out a correlation between the internal pressure, a quantity appearing in the equation of state, and the order of solubility of a given solute in a series of solvents (Reference 40). The internal pressure can be related to the cohesive energy of a substance and is defined as the increase in internal energy per mole if all intermolecular forces are eliminated. The cohesive energy per unit volume is named the cohesive energy density and was related to the behavior of specific solvents. In 1949 Hildebrand proposed the use of the term solubility parameter, which is defined as the square root of the cohesive energy density. The solubility of a material is related to its chemical structure as well as the structure of the solvent and consequently to the intermolecular forces of each substance. As a general rule similar structures favor solubility. Thus a solute with solubility parameter similar to that of the solvent is more soluble.

For low molecular weight compounds the cohesive energy can be related to the molar heat of evaporation. For materials of higher molecular weight, other methods such as solubility have been used to determine cohesive energy. A number of investigators have found that cohesive energy may be considered an additive property determined by contributions of individual groups. Thus the approximate cohesive energy and solubility parameter may be estimated on the basis of the structure of the compound. Tables of group contributions are available in the literature (References 23, 24).

There are many cases in which the solubility parameter of the solute and solvent are similar but the substances are not mutually soluble. This occurs because the solubility parameter was originally developed for those materials having dispersion (London or van der Waals) forces only. The concept thus had to be refined to take into account additional intermolecular forces including dipole-dipole interactions and hydrogen bonding. Thus the cohesive energy and solubility parameter can be separated into components corresponding to the three forces. Hensen (Reference 23) developed this technique to enable substances to be represented on a triangular graph (Figure 9) where each side represents one component of the intermolecular forces. Then solute and solvent in close proximity (i.e., where the magnitudes of the three solubility parameter components are similar) are mutually soluble, and the problem with Hildebrand's parameter disappears.

Unfortunately the additive group contributions for Hensen parameters are not as extensive as the Hildebrand group contributions, so this better portrayal can not always be applied.

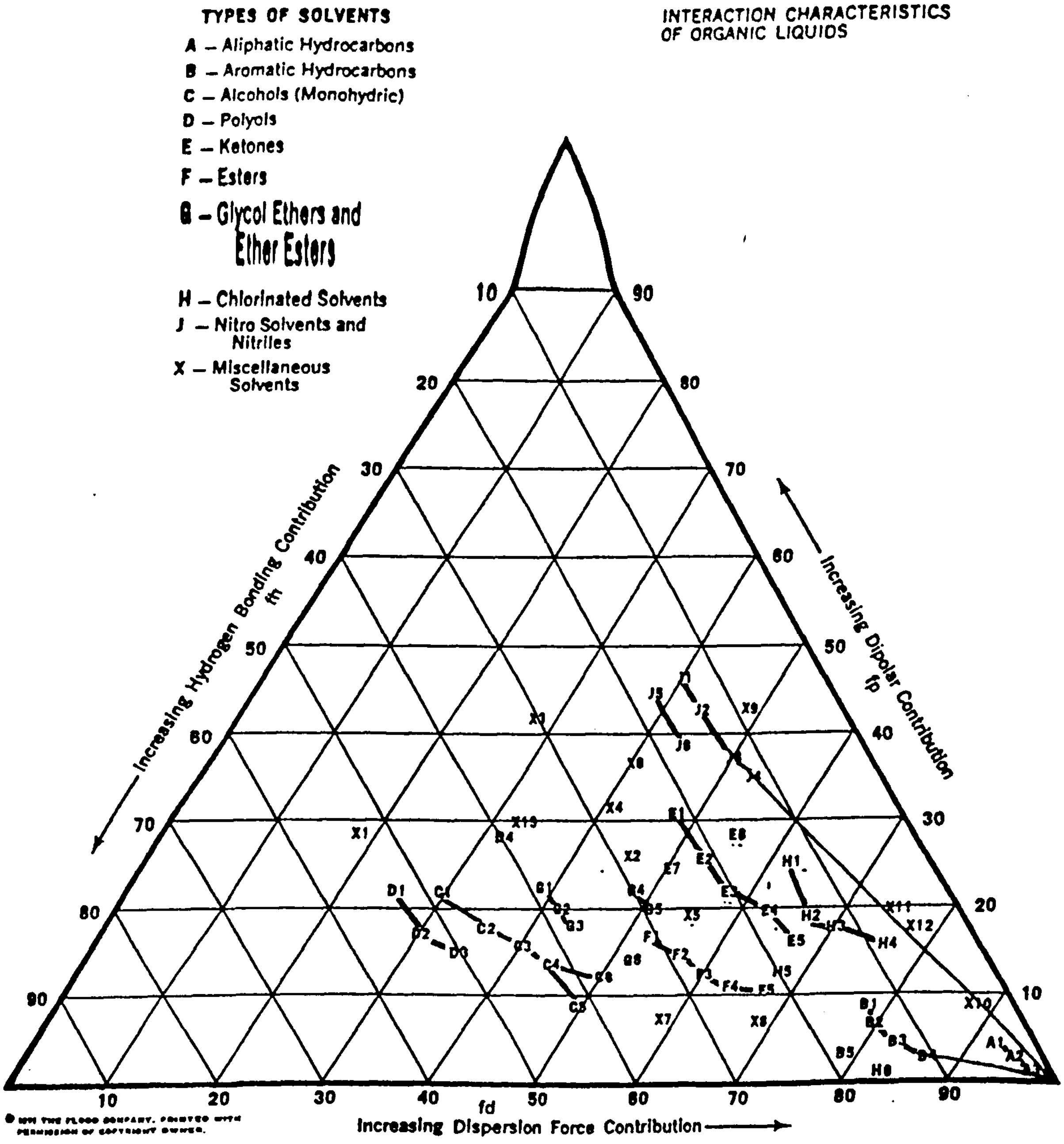


Figure 9. Hensen Diagram of Common Solvents

The interfacial tension between phases is especially important in the formation of emulsions. As interfacial tension decreases, emulsification is generally easier. The interfacial tensions of mutually soluble liquids decrease as their solubilities increase (Reference 25). Thus materials with closer solubility parameters will more easily form emulsions. However, proper emulsifying agents still are needed. Solubility parameters also have been empirically related to many other properties including HLB, surface tension, wetting and dispersion of solids.

(2) Hydrophile-Lipophile Balance (HLB)

The hydrophile-lipophile balance (HLB) of surface active molecules is useful in defining their properties in aqueous solutions and was quantified many years ago. The HLB system assigns a number to a surfactant related to the proportion of hydrophilic (water loving) and lipophilic (oil loving) groups in the molecule. The lower the HLB value the more lipophilic; and the higher the HLB value the more hydrophilic. In selecting emulsifiers, each oil to be emulsified requires a certain HLB. It is well known that in aqueous emulsification, blends of surfactants generally outperform a single emulsifier. Thus a particular emulsifier blend matching the required HLB usually will provide the most stable emulsion prepared from various combinations of the individual emulsifiers. However, the HLB approach does not identify the best types of emulsifier to be blended. Different types of emulsifier blended to the same HLB may produce a better emulsion. Also, the HLB concept provides no indication of the needed concentration, and generally it has not been applied to non-aqueous systems (Reference 26, 27).

The HLB value of a surfactant has been correlated to its solubility parameter by the following relationship:

$$\text{Solubility parameter} = 6.0-119.1/(\text{HLB}-54),$$

where the solubility parameter is expressed in $(\text{cal/cm}^3)^{0.5}$ (Reference 23)

3. DISCUSSION

a. Explosive Matrix and Simulant

The explosive matrix designated by WL/MNME for this task is TNT. This selection stemmed from problems the Air Force had encountered with AFX-644 melt-cast explosive consisting of the higher melting solid NTO and aluminum powder dispersed in a TNT/wax emulsion. Since Mach I's facilities preclude work with energetic explosives, a simulant for the TNT was required. Consideration of the nitro group to carbon ratio in TNT led to selection of NE, which has a similar ratio. Calculation of the Hildebrand solubility parameters of the two compounds (Table 29) also indicated that they should have similar solubility properties. This table lists a number of other compounds having solubility parameters close to that calculated for TNT.

TABLE 29. POSSIBLE TNT SIMULANTS

Compound	Melt Point, °C	Boil Point, °C	Calc'd. Solubility Parameter (1)	Lit.(2) Solubility Parameter (1)	Density (g/cm^3)
TNT	80	------	11.6		1.54(3)
Nitroethane	-90	114-15	11.4	11.0-11.2	1.045
Nitropropane	--	131-2	10.8	10.2	0.998
Nitrobenzene	5-6	210-11	10.7	9.8-11.1	1.253
2-Nitrotoluene	-4	25	10.3	10.5	1.163
3-Nitrotoluene	15-16	230-231	10.3	10.4	1.157
4-Nitrotoluene	52-54	238	11.2		1.392
2,4-Dinitrotoluene	67-70	------	10.8		1.321
2,3-Dinitrotoluene	59-61	------	10.6		1.263
2,6-Dinitrotoluene	64-66	------	10.7		1.283
3,4-Dinitrotoluene	54-57	------	10.6		1.259
1,2-Dinitrobenzene	117-19	319	11.1		1.368
1,3-Dinitrobenzene	88-90	300-3	11.8		1.57
1,4-Dinitrobenzene	172-74	299	12.1		1.63
Benzonitrile	-13	188	11.6	8.4-10.7	1.01
o-Tolunitrile	13	------	11.2		0.989
m-Tolunitrile	-23	------	11.1		0.976
p-Tolunitrile	26-29	------	11.2		0.981
2,6-Dicyanotoluene	135-37	------	13.5		--
Isophthalonitrile	160-62	------	14.1		--
Terephthalonitrile	224-27	------	14.1		--

(1) - (cal/cm^3)$^{0.5}$
(2) - Reference 23
(3) - liquid

Many of the listed compounds can be rejected on the basis of high melting point. Several of the nitriles have calculated solubility parameters very close to that of TNT. However, the experimental value for benzonitrile is not in good agreement with the calculated value. Consequently the calculated values of all of the nitriles may be in error due to assignment of an erroneous value for the cohesive energy of the nitrile group. In contrast, the calculated and experimental values for the nitro compounds, where available, agree well.

Initial evaluation of the Ganex resin emulsifiers at WL/MNME (Reference 28) in Phase I indicated that nitroethane performs well as a simulant. In nitroethane a blend of the three Ganex resin products in a 1/1/1 ratio appeared to perform as well as Ganex WP-660 resin emulsifier for Indramic 170C wax. However, in TNT Ganex WP-660 resin gave greater emulsion stability than the blend.

The single disadvantage of nitroethane is its low boiling point (114-115°C). Therefore, nitropropane was evaluated as a potential substitute on the strength of its higher boiling point. However, as shown in Table 29, its solubility parameter is lower than that of nitroethane or the value calculated for TNT. The ratio of nitro group to carbon is also lower (52%). As shown in Table 30, nitropropane gave less than 5 minutes stability for Indramic 170C wax with Ganex WP-660 resin compared to more than 33 minutes with nitroethane. Therefore, nitroethane was used for all the Phase I work.

TABLE 30. NITROPROPANE COMPARED TO NITROETHANE AS TNT SIMULANT

Emulsifier	Wax	Emulsion Break (min) Nitropropane	Nitroethane
Ganex WP-660	Indramic 170C	<5	>33
Ganex WP-660	Polywax 600	0.5	0.5
Ganex WP-660	Montan MD2	0.3	0.3
Ganex V-216	Indramic 170C	2	2

The corresponding mixes also differed considerably in appearance. With Polywax 600 and Montan MD2 wax the degree of separation also differed.

Later work by WL/MNME using experimental, modified Ganex resin emulsifiers showed some differences in results obtained using nitroethane versus TNT. Replication of tests with Ganex V-216 resin gave results differing from those obtained earlier. This shed doubt on the conclusion that with this emulsifier nitroethane satisfactorily simulated TNT. The simulant was then changed to 2,4-DNT which, as Table 29 shows, has a lower solubility parameter as well as a lower ratio of nitro to carbon groups. Nevertheless, results with 2,4-DNT correlated better with those obtained using TNT. Table 31 shows these data.

Table 31. COMPARISON OF EMULSION STABILITY BETWEEN SIMULANTS AND TNT

Emulsifier	TNT (1)	Emulsion Break (min) 2,4-DNT (2)	Nitroethane (2)
Ganex V-216	>25	30	2
Ganex WP-660	25	30	15
Ganex K90(3)	<5	1	30
Ganex K120(3)	<5	1	45

(1) Indramic 800 or Indramic 170C wax at 88-91°C, 3-5% emulsifier.
(2) Indramic 170C wax at 100°C, 20% emulsifier.
(3) Experimental

Although 2,4-DNT, an aromatic compound like TNT, appeared to give better correlation than nitroethane, differences persisted. As Table 31 shows, the concentration of emulsifier used with 2,4-DNT was higher than that needed for TNT. Table 32 shows that emulsion stability with 2,4-DNT simulant decreased greatly when emulsifier concentration was reduced to 5%. Note that Ganex WP-660 resin gives good stability with TNT at that level.

TABLE 32. EMULSION STABILITY USING 2,4-DINITROTOLUENE AS TNT SIMULANT

Ganex Emulsifier	Concn (2)	Emulsion Break (min)(1)
Ganex V-216	20	30
	5	3
Ganex WP-660	20	30
	5	1
Ganex K90(3)	20	1
	5	1
Ganex K120(3)	20	1
	5	1

(1) Indramic 170C wax at 100°C.
(2) Wt % based on wax.
(3) Experimental

A number of emulsifiers that had been tested earlier with nitroethane simulant were retested using 2,4-DNT. The retested emulsifiers were those that had shown some degree of stability (1 to 3 min) with nitroethane or that contained an aromatic ring. Table 33 shows the results of re-testing.

TABLE 33. COMPARISON OF 2,4-DNT AND NITROETHANE SIMULANTS WITH VARIOUS EMULSIFIERS

	Emulsion Break (min) (1)	
Emulsifier	Nitroethane	2,4-DNT
Nitrobenzoic ester of Unilin 425	<0.5	<0.5
Nitrobenzoic ester of Unilin 550	<0.5	<0.5
Phthalic half ester of Unilin 425	<0.5	<0.5

TABLE 33 (continued)

PBMA-10 Half ester of Unilin 425	3	<0.5
PBMA-10 Half ester of Unilin 700	<0.5	<0.5
PBMA-10 Half ester of Unilin 550	<0.5	<0.5
SMA 1000 ester with Exxal 12	<0.5	<0.5
PBMA-10 Poly bd R45HT Blend (1/1)	<0.5	<0.5
PBMA-10 Unithox 480 Blend (3/1)	<0.5	<0.5
PBMA-10 Kenamide S221 Blend (1/1)	<0.5 1	<0.5
SMA 2627 Igepon T-77 Blend (1/1)	1.3	<0.5

(1) Indramic 170C wax at 95-100°C.

For most of the emulsifiers tested, stabilities with 2,4-DNT were similar to those with nitroethane.

Overall, nitroethane appears to be a fairly good simulant for TNT in these studies. The simulant 2,4-DNT appears to be slightly better, probably because it contains an aromatic ring resembling that of TNT. However, neither candidate exactly duplicates the behavior of molten TNT.

Ganex resin emulsifiers provide better emulsion stability for wax in TNT than for wax in either of the simulants.

b. Waxes

At the request of WL/MNME, two wax compositions were used in Task 3:

- Indramic 170C, a microcrystalline petroleum wax that is qualified for use as a desensitizer in military explosives and is produced by Industrial Raw Materials.

- Polywax 600, a synthetic polyethylene produced by Petrolite. Several studies of the Polywax series have shown them to perform well as desensitizers in certain explosives (Reference 2).

Indramic 170C wax consists of several distinct fractions of differing molecular weight. Figure 10 shows a DSC trace obtained by WL/MNME. Three fractions covering a wide melting range are apparent. It has been suggested that the process of melting, casting, and recrystallization may fractionate the wax and cause problems in the manufacture of explosives (Reference 2).

For quality control of petroleum microcrystalline waxes MACH I suggests that WL/MNME adopt IGI Boler's gas-liquid chromatography (GLC) method (Appendix B). This method is the most sensitive to determine if the supplier changes processing or crude source and to identify potential problems at the earliest possible time.

The Boler GLC analysis measures the normal and isoparaffin content for each carbon number present. This is illustrated by the analysis of their Petrowax 9508 microcrystalline wax shown in Figure 11. The isoparaffin content of the C_{20} and C_{63} wax is fifty percent (Figure 12). There are no isoparaffins in the C_{26}—C_{34} fraction. This suggests that a fully refined (normal) paraffin wax was blended with the higher melting microcrystalline wax fraction. The higher the melting point of the microcrystalline wax, the greater the isoparaffin content. The high isoparaffin content at the lowest carbon numbers suggests that a small amount of slack (i.e., oil-containing) wax may have been incorporated to meet a penetration specification.

Polywaxes are synthetic straight carbon chain (i.e., unbranched) polyethylene waxes. Petrolite cites a melting point of 94°C by ASTM D-127 for Polywax 600. Using the Fisher-Johns apparatus, MACH I determined the melting point to be 88°C. The DSC trace shown in Figure 13 reveals a uniform, narrow melting range unlike that of Indramic 170C wax.

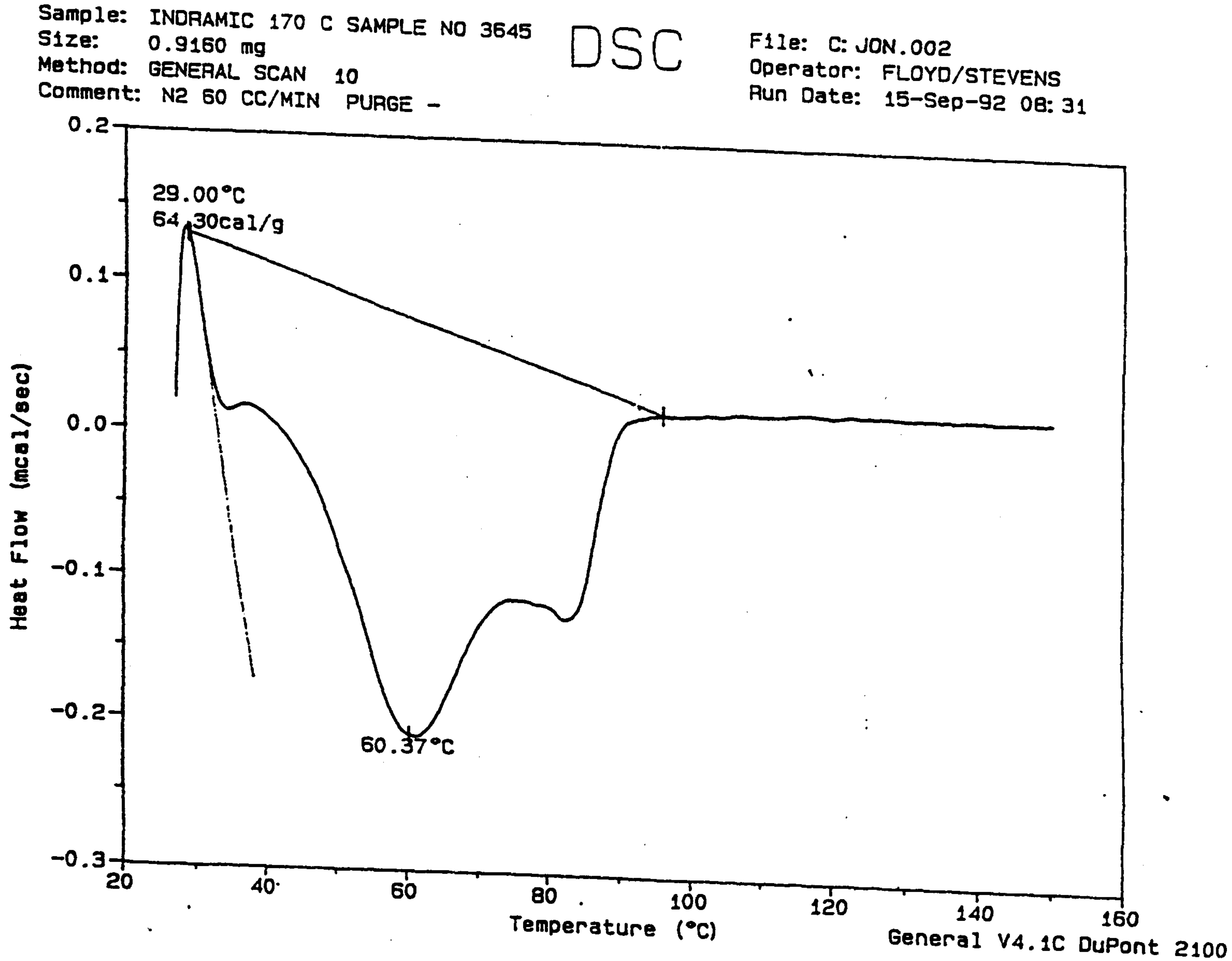


Figure 10. DSC Of Indramic 170C Wax

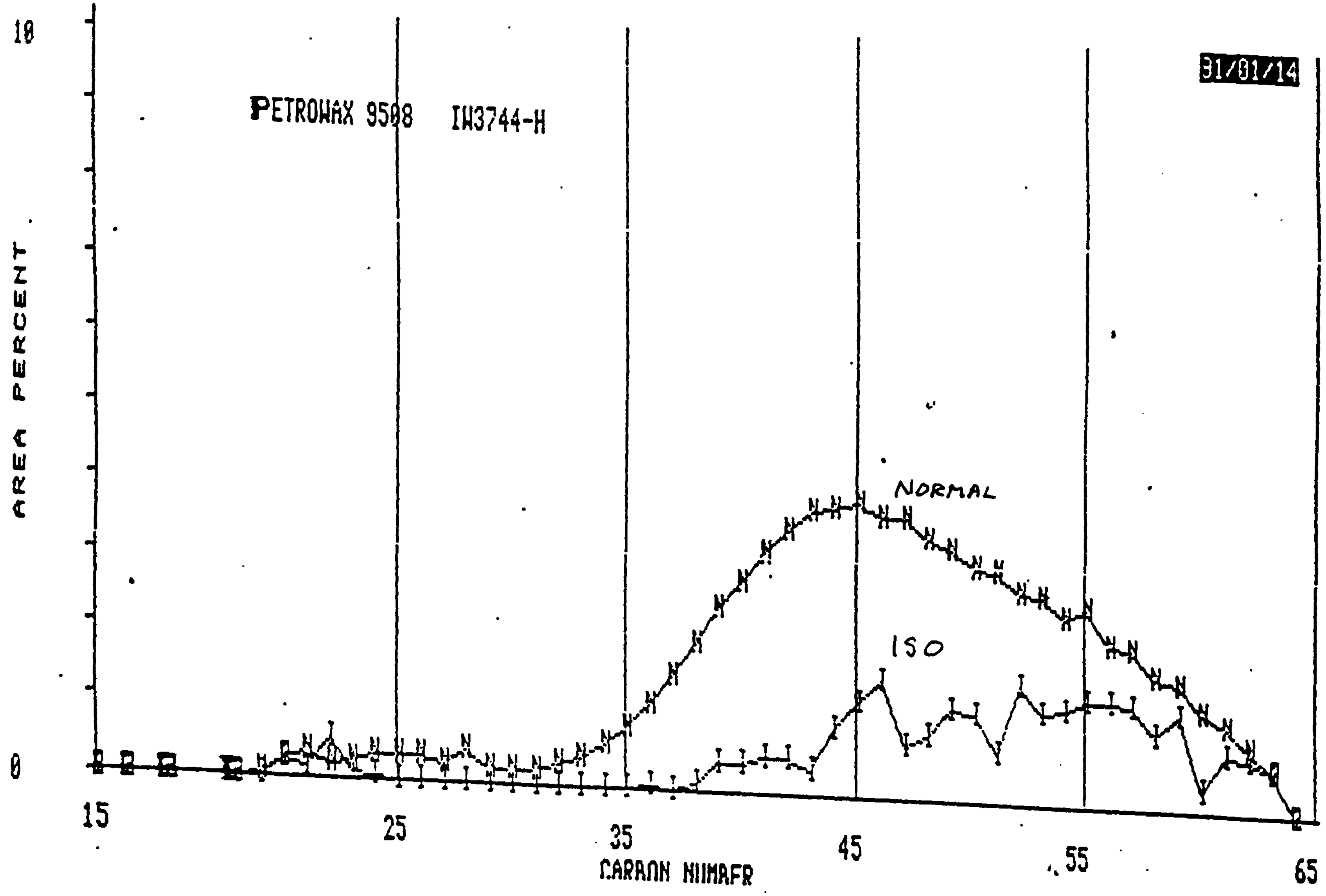


Figure 11. GLC Analysis Of Petrowax 9508

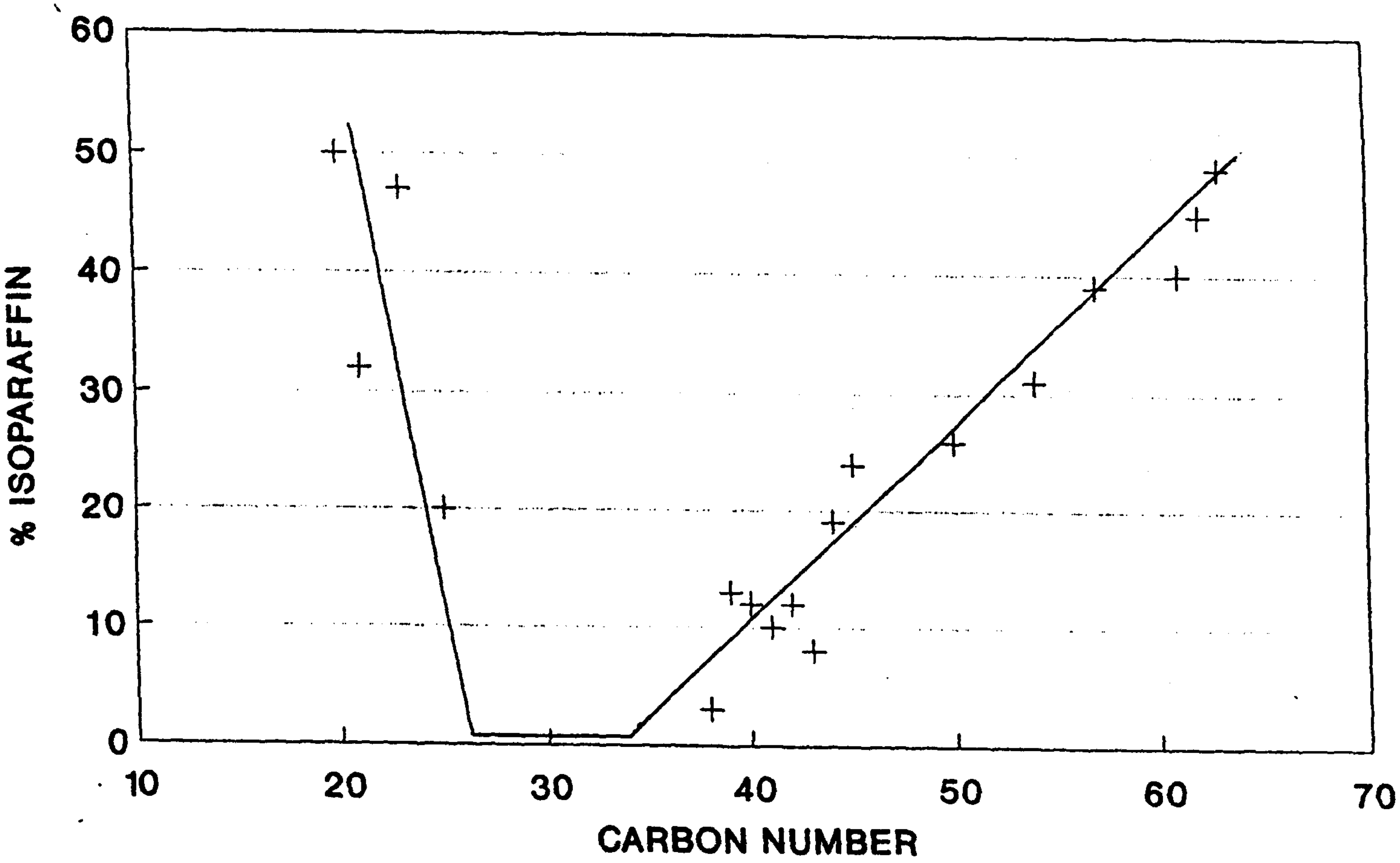


Figure 12. Isoparaffin Content Versus Carbon Number, Petrowax 9508

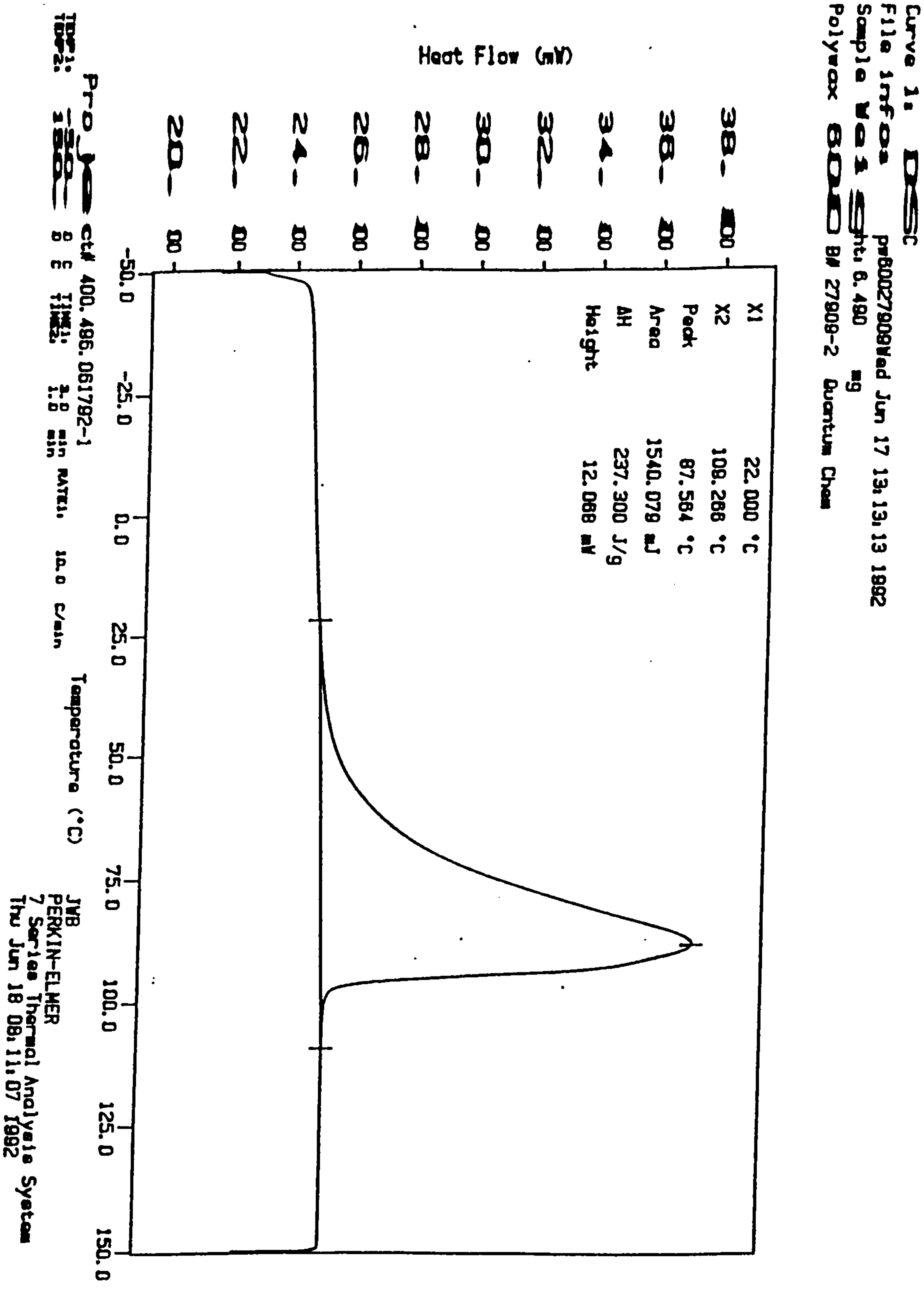


Figure 13. DSC Of Polywax 600

Table 34 summarizes key properties of these two waxes.

TABLE 34. SELECTED PROPERTIES OF WAXES USED IN THIS STUDY

Wax	Melt Pt. (°C)(1)	Specific Heat (cal/g/°C)	Heat Of Fusion (cal/g)	Solubility Parameter (2)
Indramic 170C	83-5	0.43	40	8.3
Polywax 600	94	0.5	56	8.8

(1) ASTM D-127
(2) $(cal/cm^3)^{0.5}$

WL/MNME has used Indramic 800 wax in much of their work. This wax melts slightly higher (87°C) than Indramic 170C (≈84°C) but performs similarly in emulsion stability testing as shown in Table 35.

TABLE 35. EMULSION STABILITY USING INDRAMIC 800 WAX AND INDRAMIC 170C WAX WITH NITROETHANE

Emulsifier	Wax	Emulsion Stability Break Time (min)
Ganex WP-660	Indramic 170C	10
Ganex WP-660	Indramic 800	10
Ganex WP-660/ Ganex V-216 (1/1)	Indramic 170C	10
Ganex WP-660/ Ganex V-216 (1/)	Indramic 800	5

c. Wax Substitutes

The objective of this phase of Task 3 is to identify wax substitutes for use in TNT melt-cast systems. These substitutes must meet performance criteria cited earlier, namely: miscibility, stability, compatibility, desensitizing effectiveness, long-term availability, and consistent composition.

Each substitute must possess one or more properties conducive to desensitizing TNT explosives. The solubility parameter of each candidate was estimated. Those with solubility parameters closer to that of TNT and other energetic ingredients than that of wax were selected. Thus the candidates would be expected to wet particulate ingredients such as TNT, RDX, HMX, and aluminum better than petroleum wax does. They should fill more voids, reduce air entrapment, and lubricate friction points. To facilitate processing, their viscosity must not increase that of the molten explosive mixture. These properties are expected to enhance desensitization.

Even if a promising candidate wax substitute appears not to require a dispersant for emulsion stability, incorporation of an effective surfactant (e.g., a member of the Ganex resin family) may improve dispersion of particulates. This important benefit has been demonstrated in Phase I of this program (suspensions of aluminum powder), in a PBX (Reference 29), and in industrial applications (Appendix A).

Using only 0.2% Ganex V-216 or V-220 resin in a modified AFX-931 PBX general purpose bomb explosive, ARC achieved a tenfold reduction in end-of-mix viscosity. Two successive pint mixes processed so well that the two-hour holding period usually necessary to obtain a castable mix was eliminated. The dramatic improvement, which was confirmed in mixes at the one-gallon scale, offers a route to increased solids loading, hence higher energy (Reference 29). Had a wax been used, there is little doubt that the lowered viscosity would have improved coating of particulates and desensitization. The cited work by ARC was performed for MACH I outside the present contract.

4. EMULSIFIERS

In Phase I of this program several outstanding emulsifiers were developed for the TNT/wax melt-cast system. Ganex resin emulsifiers provided excellent emulsion stability for several petroleum waxes and some stabilization with the synthetic Polywax 600. Table 36 shows test results obtained at WL/MNME in mixes with TNT.

TABLE 36. MISCIBILITY RESULTS USING GANEX EMULSIFIERS WITH TNT

Wax	Separation (mL) (1) Ganex WP-660	Ganex V-220
Indramic 800	0.0	0.0
Montan	1.3	1.1
Paraflint C1	0.4	0.05
Paxwax 7517	0.0	0.2
Petrowax 9508	0.0	0.2
Polywax 600	1.2	1.1
Reed Wax 6884	0.2	0.2

(1) Separation after 20 min with 15 wt.% emulsifier based on wax.

Ganex WP-660 resin provided excellent stability with Indramic 800, Petrowax 9508 and Paxwax 7517. This emulsifier was tested at lower concentrations, and it permitted no layer separation with any of these waxes at concentrations as low as 0.5% based on wax. To build on these promising results MACH I requested the supplier to provide several modified forms of the Ganex resin emulsifiers. MACH I reacted a Ganex resin emulsifier with acids to form ion pairs. Such modifications were expected to enhance emulsion stability or help overcome future problems.

Since the nitrogen in Ganex resin surfactants may be a major factor in their effectiveness, a logical second approach to identifying suitable emulsifiers included examining a series of amine salts of sulfonic acids, carboxylic acids, and partial esters of phosphoric acid. The reaction employed to prepare these salts is rapid at room temperature. It is easy to measure the exotherm that confirms reaction and to detect an excessive exotherm that might cause difficulty in scaled up production. There are few suitable, commercial amine salts. Therefore selected compounds were synthesized to provide the wide range in polarity needed for screening as emulsifiers.

A number of ashless motor oil detergents are also based on nitrogen-containing surfactants or polymers. Therefore, these materials were also selected for evaluation. Several of these variants were synthesized by Lubrizol especially for this program.

Also included were recently commercialized *N*-alkyl pyrrolidones which provide excellent water/oil emulsions. In addition, a variety of other nitrogen-containing surfactants and emulsifiers were selected for testing.

The third approach was to select candidate emulsifiers on the basis of solubility parameter closest to that of TNT. This was done in Phase I of the program. Technologists seeking surfactants for compatibilizing polymer blends often take this approach. They commonly select surfactants consisting of block copolymers of monomers contained in the polymers to be compatibilized (Reference 30). In the present program MACH I selected esters of nitrobenzoic acid to evaluate this concept. Other types of surfactants that were selected using this method were esters of polybutadiene-maleic polymers and esters of styrene-maleic copolymers.

In a variation of this approach MACH I used the HLB concept to select a variety of surfactants as candidate emulsifiers. As discussed in Section V.2.b. of this report, HLB and solubility parameter are related, with HLB allowing a finer adjustment in the solubility parameter. A number of polyethoxylates were selected to evaluate this concept.

Also evaluated as emulsifiers or co-emulsifiers were coupling agents, solvent/plasticizers such as fatty amides and aromatic phosphate esters commonly used as plasticizing fire retardants. Block copolymers such as styrene- polybutadiene-styrene offered the potential of end-group compatibility with NE and TNT and middle group compatibility with wax.

Several surfactants were also selected to check claims in the literature of successful use as emulsifiers in explosive compositions.

a. Synthesis of Emulsifiers

(1) Synthesis of Amine Salts for Wax Emulsifiers

Amines react rapidly at room temperature with organic sulfonic acids and carboxylic acids. A 3% excess of amine was used to ensure that there would be no free acid in the product. Eighty-gram mixes were made in a 130 mL specimen jar by first adding the amine, then adding the acid and immediately stirring with a 1-inch Jiffy mixer blade. Liquids were reacted at room temperature. Solid ingredients were melted before reaction. The exotherm varies from about 10-60°C.

(2) Synthesis of Nitrobenzoic Acid Esters

Ethyl *p*-nitrobenzoate (8.9 g) was charged into a round-bottom flask fitted with a nitrogen purge, thermometer and a distilling head. Unilin 550 alcohol (31.1 g) and 0.1 grams of Fascat 4102 were added. The temperature was raised to 140-5°C and stirred under a slow nitrogen purge while ethanol was distilled off. When the stoichiometric quantity of ethanol was removed (4 hrs.), the reaction was terminated. The Unilin 425 ester was prepared by the same procedure.

(3) Synthesis of Styrene-Maleic Copolymer Half Esters

Styrene-maleic Copolymer SMA 1000 (27.4 g) was charged to a round-bottom flask fitted with a nitrogen purge and thermometer. Exxal 12 (22.1 g), a dodecyl alcohol, was added and the mixture was heated to 155°C with occasional stirring for 2 hours, during which time the mixture became a uniform melt. All of the styrene-maleic acid esters were made by a similar procedure (Reference 31).

(4) Synthesis of Polybutadiene-Maleic esters

To polybutadiene-maleic polymer PBMA-10 (10 g) was added 5.45 grams of Unilin 425 alcohol. The mixture was heated to 140°C with stirring for one hour, during which time the mixture became homogeneous. All of the esters were made by a similar procedure (Reference 32).

(5) Synthesis of Phthalate Half-Esters

Phthalic anhydride (5.07 g) and 14.9 grams of Unilin 350 alcohol were charged to a container and heated with stirring for 2 hours at 106-110°C. The mixture became a uniform liquid during this time. All of the phthalate esters were made by a similar procedure.

SECTION VI

EVALUATION OF WAX SUBSTITUTES

1. SUMMARY

The objective of this phase of Task 4 is to evaluate selected wax substitutes for use in TNT melt-cast systems. As stated in Section III of this report, the following criteria were developed for selection of candidate improved desensitizers:

- Miscibility with molten TNT
- Wetting of explosive crystals
- Melting range generally below 98°C
- Chemical compatibility with the explosive
- Viscosity below 10,000 cP at melt temperature
- High enthalpy (high specific heat and heat of fusion or transition)
- Moderate strength and modulus
- Reproducible properties
- Assured availability
- Low cost

Instead of the minimum of four contractually required substitutes, MACH I submitted 16 candidates, each with an effective emulsifier, to WL/MNME for evaluation with TNT. At WL/MNME 11 of the candidates passed tests for compatibility (DSC) and emulsion stability.

The following four candidates were found to be soluble in molten TNT:

- Triphenylphosphate (TPP)
- Arconate
- Santicizer 148
- TPP/A-C 400 blend.

The best emulsions were formed by:

- Kenamide S180/Ganex WP-660
- Nipol 1312
- Nipol 1312 lv.

The next best, all using Ganex WP-660 resin emulsifier, were:

- Telura 343
- Kenamide E
- Kenamide S
- Santicizer 148/Kraton D1101 blend

MACH I recommends use of a Ganex resin surfactant with all candidates, even if not required to achieve a stable emulsion.

First, Ganex resin surfactants excel in stabilizing emulsions of all of the candidates that require a stabilizer. Second, these surfactants provide a number of important additional benefits:

- Wetting of particles
- Dispersion of particles
- Reduction of friction
- Reduction of viscosity
- Increased density by reduction of trapped air
- Filling of voids
- Greater desensitization
- Increased production rate for TNT melt casting and PBX
- Higher attainable solids loading.

2. EVALUATION PROCEDURE

The standard test for emulsion stability at 90-100°C was used to assess miscibility of the candidate wax substitute with TNT simulant. In some cases the procedure was modified by: (1) omission of emulsifier or (2) melting the emulsifier in the wax substitute before addition of the nitroethane simulant. Such modifications are noted in following text and tables. Probable desensitizing effectiveness was estimated using the selection criteria and desensitization mechanisms presented in Section III of this report.

3. RESULTS OF EVALUATION TESTS

a. Low Molecular Weight Compounds

(1) Amides

Table 37 shows the properties of four wax-like amides manufactured by Witco that are based on straight chain saturated and unsaturated naturally occurring monobasic fatty acids and amines. Values in parentheses are estimated (Reference 24).

TABLE 37. PROPERTIES OF AMIDE COMPOUNDS EVALUATED AS WAX SUBSTITUTES

Amide	MP (°C)	Specific Heat cal/g-°	Heat of Fusion (cal/g)	Solubility Parameter $(cal/cm^3)^{0.5}$
Stearamide	98-108	(0.42)	44	(9.8)
Erucamide	76-86	(0.42)	29	(9.7)
Stearyl Stearamide	92-95	0.36	31	(9.0)
Erucyl Stearamide	76-80	0.48	31	(9.0)

The melting points of the amides are in the proper range, and their viscosities in the molten state are favorably low. The thermal properties of the amides suggest good absorption of heat. The heat of fusion of stearamide is slightly higher than that of wax while those of the others are slightly lower.

The specific heats of all of these amides are similar to that of Indramic wax; thus the benefit this mechanism of heat absorption from hot spots should be essentially unchanged.

The predicted solubilities of all of the amide substitutes in TNT suggest that they will be superior to wax in filling the microvoids of cast TNT. Because these compounds (like RDX, HMX, and NTO) have solubility parameters near or above that of TNT, they should exceed wax in wetting particulate explosive ingredients. Wetting depends strongly on cohesion parameters of the components and is integrally related to their solubility parameters.

The viscosity of a melted explosive containing solid energetic material may also be lowered by a wax substitute having greater solubility and providing better wetting. This could allow higher solid loadings or facilitate processing.

The mechanical properties of explosives prepared with the low molecular weight amide candidates are expected to be similar to those produced by wax. Increased strength or improved elastic properties of the explosive are not anticipated.

The amides are known for their lubricity and serve as commercial lubricants. Since they are likely to be better dispersed and to wet other energetic components well, they may excel wax in desensitizing by reducing interparticle friction.

As shown in Table 38, the amides proved to be miscible with the nitroethane simulant at the test temperature without added emulsifiers.

TABLE 38. EMULSION STABILITY PROVIDED BY AMIDE WAX SUBSTITUTES IN NITROETHANE

Amide	Trade Name	Stability, min
Stearamide	Kenamide S	>60
Stearyl Stearamide	Kenamide S-180	>60
Erucyl Stearamide	Kenamide S-221	>60
Erucamide	Kenamide E	>60

All of the amides (in specimens 521A-D, shown in Figure 14 in the order listed in Table 38) gave clear solutions with nitroethane at the test temperature. Note the contrasting, milky appearance of specimen A267, which contains synthetic polyethylene wax (Polywax-600) emulsified with Ganex-WP660 resin.

On cooling to room temperature, the amide systems gave uniform solid yellowish (stearamide, 521-A) or white plugs (Figure 15).

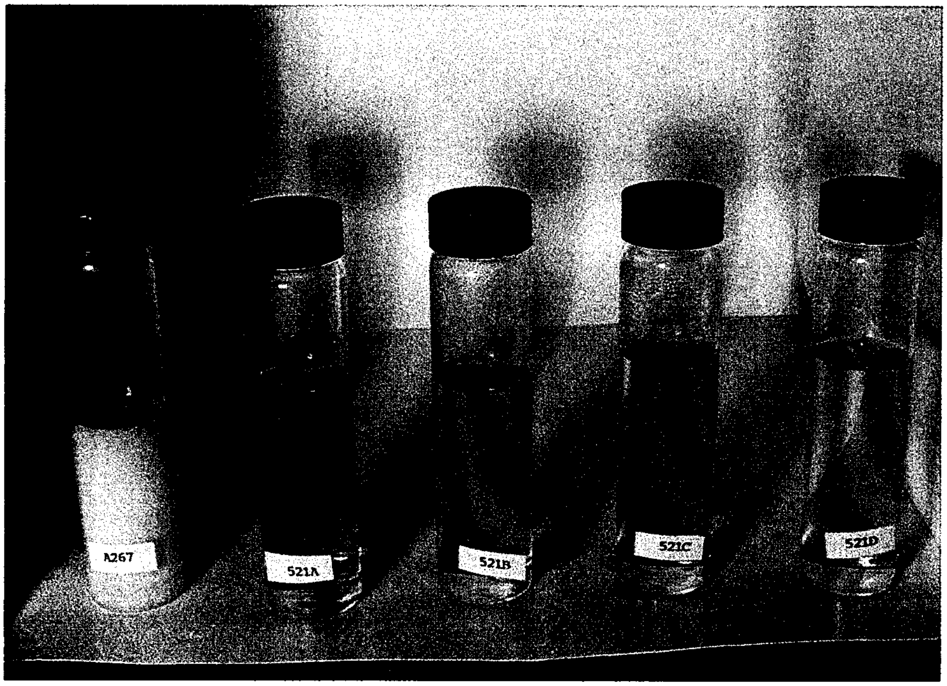


Figure 14. Amide Wax Substitutes and Nitroethane at Test Temperature

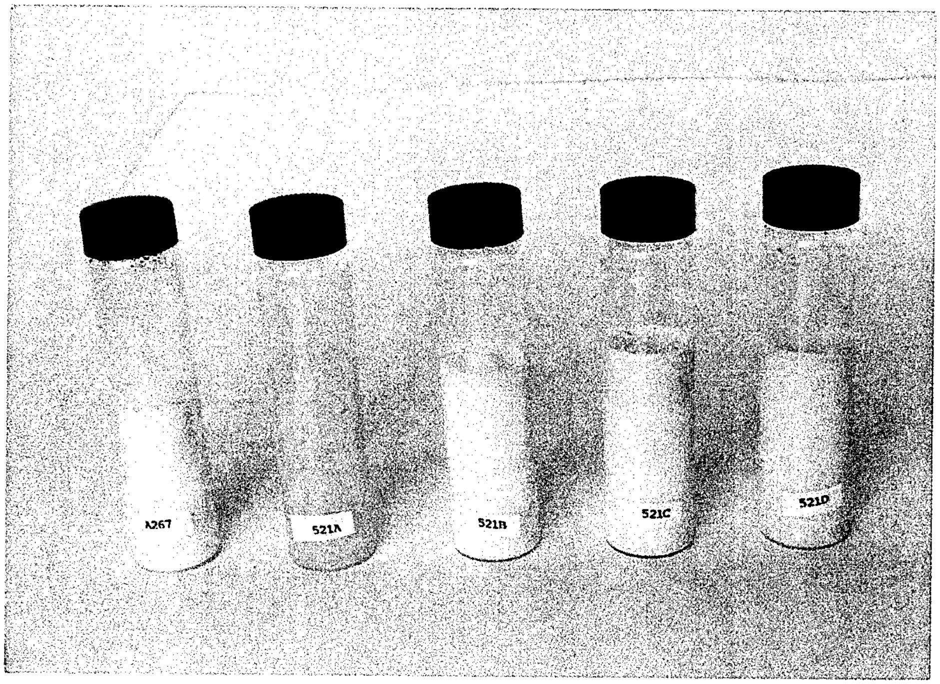


Figure 15. Amide Wax Substitutes and Nitroethane at Room Temperature

Energetic components other than TNT in an explosive formulation may require an emulsifier. As shown in Table 39, stable emulsions were achieved with combinations of the amides and a variety of emulsifiers.

TABLE 39. EMULSION STABILITY ACHIEVED WITH AMIDES AND VARIOUS EMULSIFIERS

Amide	Emulsifier	Break Time, (min)
Stearamide	Ganex V-216	>200
Stearamide	Ganex V-220	200
Stearamide	Ganex WP-660	200
Stearyl Stearamide	Ganex WP-660	210
Stearyl Stearamide	Ganex V-216	180(1)
Stearyl Stearamide	Lubrizol 2633	>60
Stearyl Stearamide	Lubrizol 2631	60
Stearyl Stearamide	Lubrizol OS 87440A	>240
Stearyl Stearamide	Lubrizol OS 22277AJ	60
Stearyl Stearamide	LOA-565	>120
Stearyl Stearamide	Hi Tech 644	>120
Stearyl Stearamide	Hi Tech 646	>120
Stearyl Stearamide	Acryloid 956	>120
Erucyl Stearamide	Ganex WP-660	210
Erucyl Stearamide	Ganex V-216	180

(1) Emulsifier and wax melted before adding nitroethane.

However, as shown in Table 40, several candidate emulsifiers caused phase separation and must be rejected.

TABLE 40. EMULSIFIERS CAUSING PHASE SEPARATION

Amide	Emulsifier	Break Time, (min)
Stearyl Stearamide	Lubrizol 47550W	0.5
Stearyl Stearamide	Paraloid 106	0.5
Stearyl Stearamide	Acryloid 917T	0.5

Lubrizol 2633 is a polyolefinamide alkeneamine, a cyclic succinimide with structure somewhat similar to that of the Ganex resin emulsifiers. Lubrizol OS 87440A is a derivative of Lubrizol 2633. Lubrizol OS 47550W is a polyolefin aminoester/salt. Lubrizol OS 22777AJ is a copolymeric ester viscosity index improver. Lubrizol 2631 is an oil-soluble calcium sulfonate dispersant used in motor oil and paint. DuPont's Lube Oil Additive 565 is a copolymer containing diethylaminoethyl methacrylate and is used as a lube oil dispersant. Ethyl's Hi Tech 644 and 646 are polymers containing the succinimide group. Rohm and Haas' Paraloid 106 is a processing aid; their Acryloid 917T and 956 are polyester viscosity improvers grafted with vinyl pyrrolidone. As Figure 16 shows, Acryloid 956 gave a clear solution in Kenamide S180 (494) at the test temperature while Acryloid 947T produced a cloudy suspension that rapidly separated (Figure 17).

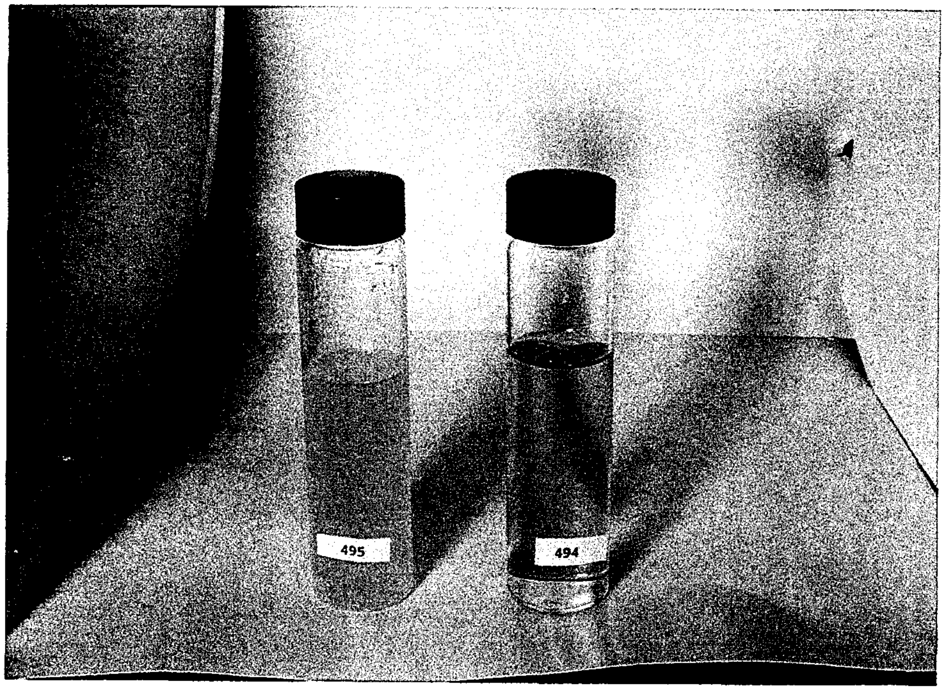


Figure 16. Acryloid 956 and 917T in Kenamide S180 Wax Substitute At Test Temperature After Shaking

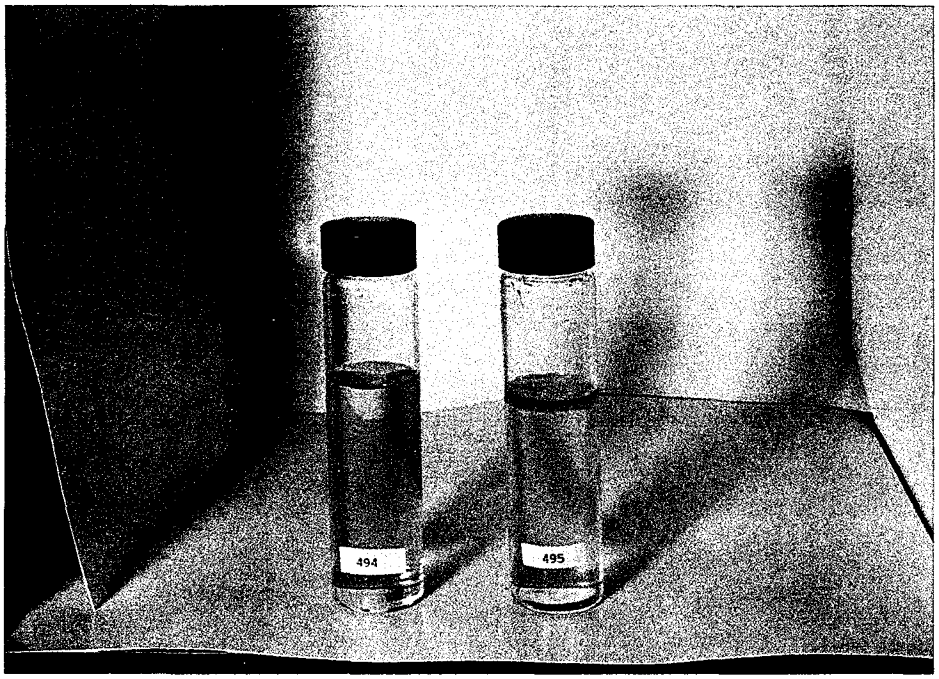


Figure 17. Acryloid 956 and 917T in Kenamide S180 Wax Substitute At Test Temperature On Standing

Figure 18 shows these emulsions after cooling to room temperature.

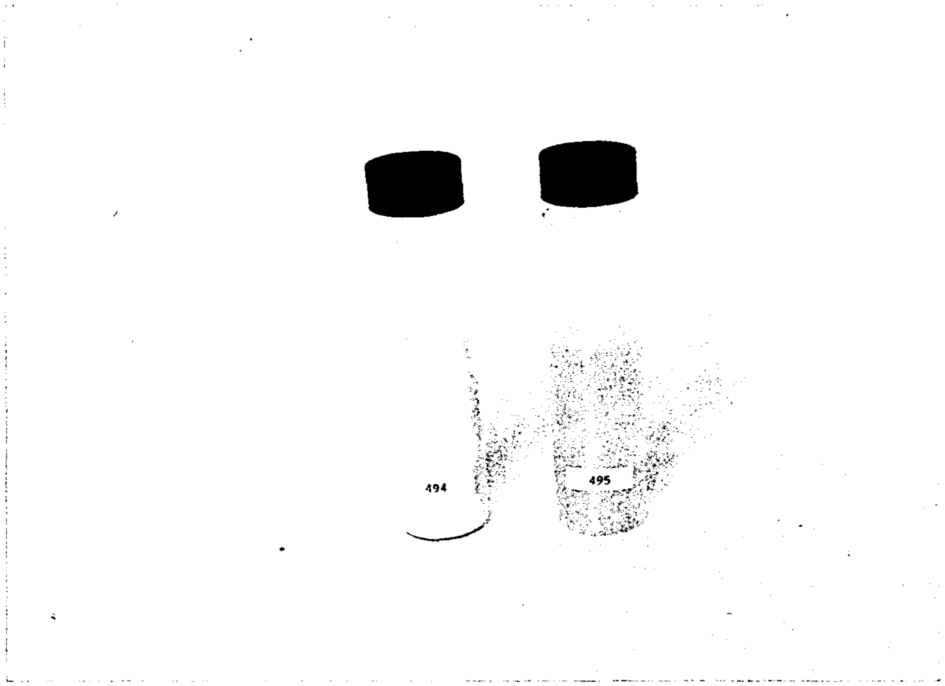


Figure 18. Acryloid 956 and 917T in Kenamide S180 Wax Substitute At Room Temperature

(2) Other Wax Substitutes of Low Molecular Weight

Five other low molecular weight materials provided emulsion stability with TNT simulant: propylene carbonate from ARCO Chemical, triphenyl phosphate from Monsanto, tricresyl phosphate from Shell, hydroxyhexylamine-alkylbenzenesulfonate from Mach I and a naphthenic process oil from Exxon. Selected properties of these compounds are shown in Table 41. Values in parentheses are estimated.

TABLE 41. PROPERTIES OF LOW MOLECULAR WEIGHT WAX SUBSTITUTES

Chemical	MP (°C)	Specific Heat (cal/g/°C)	Heat of Fusion (cal/g)	Solubility Parameter (1)
Propylene Carbonate	-49	(0.4)	--	13.3
Triphenyl Phosphate	50	(0.4)	19	(11.1)

TABLE 41 (continued)

Tricresyl Phosphate	--	(0.4)	--	(9.9)
Naphthenic Process Oil	-21	(0.4)	--	(8.0)
Hydroxylhexylamine-alkylbenzene-sulfonate	--	--	-	(9.5)

(1) $[(\mathrm{cal/cm3})^{0.5}]$.

These compounds have specific heats only slightly lower than those of the best waxes and should absorb heat adequately. All except triphenyl phosphate are liquids and thus cannot absorb heat by fusion. Triphenyl phosphate has a lower heat of fusion than wax, but its established flame retardancy may contribute to desensitization. Tricresyl phosphate, a mixture of isomers, may perform similarly. Because these wax substitutes have solubility parameters closer to that of TNT, they may fill microvoids as well as wet and coat energetic solids better than paraffin waxes.

Viscosities of the explosives containing these wax substitutes should be low, allowing better wetting and possibly permitting higher solids loading. These substitutes for wax are unlikely to increase the mechanical strength of explosives, but they may reduce brittleness.

Exudation is a problem associated with low melting waxes; the degree depends on melting point (Reference 3). The tendency to be exuded probably stems from the large difference in solubility parameter of paraffin wax relative to explosive. Since the candidate substitutes cited above are more polar than paraffin wax, they may be less subject to exudation. However, this possibility and general suitability must be verified experimentally.

The miscibilities of these compounds with nitroethane are shown in Table 42.

TABLE 42. MISCIBILITY OF THE LOW MOLECULAR WEIGHT COMPOUNDS WITH NITROETHANE

Chemical	Trade Name	Emulsifier	Break Time, (Min.)
Propylene Carbonate	Arconate	Ganex WP-660	>150

TABLE 42 (continued)

Triphenyl Phosphate	TPP	Ganex WP-660	30
Tricresyl Phosphate		----	>60
Hydroxyhexylamine-alkylbenzene-sulfonate	Ultrawet A 101	-----	>360
Naphthenic Process Oil	Telura 343	-----	>240

All of these compounds gave good emulsion stability; three of them were completely miscible with nitroethane and thus required no emulsifier at the test temperature.

b. Wax Substitutes of Higher Molecular Weight

In many propellant and explosive formulations polymers have been used successfully as binders and desensitizers. In melt-cast explosives, polymeric additives must not only be dispersible but also must exhibit manageable viscosity. Excessive viscosity impedes dispersion and practical processability. The viscosity barrier proved to be the most limiting for most candidate polymers. As Table 43 shows, the melt viscosity of a polymer must be lower than 9,000 cP to permit mixing in the test. Solubility of the polymer in the simulant is another important factor. Increased solubility of the polymeric wax substitute in the simulant permits higher melt viscosity.

TABLE 43. PROPERTIES AND STABILITY TEST MIXING OF POLYMERIC WAX SUBSTITUTES

Polymer	Trade Name	MP Soften. Pt. °C	Estimated Viscosity cP@100°C	Est. Sol. Param.(1)	Mixes in Test
Polyethylene	Polywax 600	92	15	8.8	Y
Ethylene/propylene	Petrolite CP-7	96	78	8.8	Y
Ethylene/olefin	Vybar 103	72	290	8.9	Y
Oxidized polyethylene	AC-656	98	740	8.9	Y

TABLE 43 (continued)

Butadiene/ acrylonitrile	Nipol 1312lv	-45	1000	10.1	Y
Butadiene/ acrylonitrile	Nipol 1312	-39	1500	10.1	Y
Ethylene/ vinyl acetate	AC-400	95	2200	8.8	N,Y
Ethylene/ acrylic acid	AC-5120	92	2600	9.2	Y
Ethylene/ acrylic salt	Aclyn 295	99	9000	*	N
Propylene/ butene	Eastoflex D139	85	9600	8.1	N
Ethylene/ acrylic salt	Aclyn 285	82	11000	*	N
Ethylene/ propylene	Trilene C	-55	59000	8.1	N
Ethylene/ propylene/ butene	Eastoflex D147	98	64000	8.2	N
Ethylene/ methyl acrylate	EMAC 2220	83	75000	8.9	N
Ethylene/ methyl acrylate	EMAC 2260	76	120000	9.0	N

(1) $[(\mathrm{cal/cm}^3)^{0.5}]$.

(1) Polyethylenes and Modified Polyethylenes

Several unmodified and modified polyethylene waxes similar to Polywax 600 were evaluated. The polyethylene A-C 617 is manufactured by Allied Signal and the Epolene polyethylenes by Eastman Chemical. Petrolite and Ceramer products are supplied by Petrolite. Properties of these polymers are shown in Table 44.

TABLE 44. POLYETHYLENE POLYMERS AS CANDIDATE WAX SUBSTITUTES

Polymer	Trade Name	MP or Soften. Pt.(°C)	Specific Heat (cal/g/°C)	Solubility Parameter (1)	Acid No.
Polyethylene	A-C 617	101(2)	0.5	8.8	--
Polyethylene	Epolene *N*-34	103(4)	0.5	8.8	--
Oxidized polyethylene	A-C 656	98(2)	0.5	8.9	16
"	Epolene 14	104(4)	0.5	8.9	16
"	Epolene 15	100(4)	0.5	8.9	16
"	Petrolite C-7500	97(3)	0.5	8.9	15
"	Petrolite C-8500	95(3)	0.5	8.8	9
"	Petrolite C-9500	94(3)	0.5	8.9	31
Grafted Polyethylene	Ceramer 67	93(3)	0.45	9.0	48
"	Ceramer 1608	77(3)	0.45	9.1	160

(1) $[(cal/cm^3)^{0.5}]$.
(2) ASTM D-3954.
(3) ASTM D-127.
(4) ASTM D-36.

The two unmodified polyethylenes differ from Polywax 600 in extent of chain branching. In respect to desensitizing capability the unmodified and modified polyethylene polymer waxes are expected to resemble Polywax 600, but they may differ in emulsifiability. The main commercial applications of the modified polymers depend on their easier emulsification in aqueous systems. Therefore it appeared worthwhile to learn whether these products also would provide more stable emulsions in TNT simulant. Although the solubility parameters of the waxes do increase with acid functionality (degree of oxidation), the increase may be due largely to hydrogen bonding forces that may not aid in emulsification with the simulant. The high solubility parameter of nitroethane results primarily from dipole-dipole interaction. These polymers can be expected to fill microvoids and coat the energetic particles about as well as wax does.

These polyethylene waxes should have similar heat absorption capability since their specific heats and heats of fusion are similar to those of Polywax 600.

The melt viscosities of these products are below 600 cP, and they have melting or softening points suitable for the melt-cast process.

The mechanical properties of the resulting explosives would be expected to be similar to the explosives made with paraffin waxes.

Table 45 shows the results of emulsion stability test conducted using these wax substitutes.

TABLE 45. EMULSION STABILITY USING UNMODIFIED AND MODIFIED POLYETHYLENE WAXES

Polymer Trade Name	Emulsifier	Break Time, (min)
A-C 617	Ganex WP-660	0.5
Epolene N-34	Ganex WP-660	1.0
Epolene N-34	Ganex V-216	0.5
A-C 656	Ganex WP-660	1.0
Epolene E-14	Ganex WP-660	1.0
Epolene E-14	Ganex V-216	5.0
Epolene E-15	Ganex V-216	1.0
Epolene E-15	Ganex WP-660	1.0
Petrolite C-7500	Ganex WP-660	0.5
Petrolite C-8500	Ganex WP-660	0.5
Petrolite C-9500	Ganex WP-660	5.0
Ceramer 67	Ganex WP-660	0.5
Ceramer 1608	Ganex WP-660	5.0

Polywax 600 gives break times of 3-5 minutes under similar conditions. Thus it appears that the modifications to polyethylene do not appreciably increase the stability of the emulsions with nitroethane simulant.

(2) Ethylene/Olefin Copolymers

Several polymers made by copolymerizing ethylene with other olefins were also chosen for evaluation. The Petrolite and Vybar materials are manufactured by Petrolite. The Trilene polymers are produced by Uniroyal, and Flexomer polymers are made by Union Carbide. Eastoflex polymers are manufactured by Eastman. Selected properties of these polymers are listed in Table 46.

TABLE 46. PROPERTIES OF ETHYLENE COPOLYMERS

Copolymer	Trade Name	MP Soften. Pt.(°C)	MW	Est. Sol. Parameter (1)
Propylene	Petrolite CP-7	96 (2)	650	8.8
Propylene	Trilene CP80	-55	7200	8.8
Butene	Eastoflex D139-3	85 (3)	--	8.8
Propylene/ butene	Eastoflex D-147-5	98 (3)	--	8.8
Propylene/ Diene	Trilene MB	--	--	8.9
Propylene/ Diene	Flexomer DEFD 1015	65 (4)	--	8.9
Higher Olefin	Vybar 103	72 (3)	2800	8.9

(1) $[(cal/cm^3)^{0.5}]$
(2) ASTM D-127
(3) ASTM E-28
(4) DSC

These polymers melt over a suitable range, but their melt viscosities are uncomfortably high. Their solubility parameters indicate that these polymers might give microvoid filling and wetting similar to those provided by the waxes.

The ethylene-olefin copolymers are more flexible than polyethylene polymers and might improve mechanical strength of explosives by reducing brittleness. The Eastoflex copolymers have tensile strengths of only 100–200 psi, but with greatly increased elongation (100-250%). The diene terpolymers are stronger (950 psi tensile) with reduced (80%) elongation.

The quenching of hotspots will not be as good with these copolymers as with waxes. Specific heat may be similar to waxes but the heats of fusion for these amorphous polymers will be negligible.

The high melt viscosity of these polymers thwarted attempts to compatabilize and emulsify them with nitroethane (Table 47). Several emulsifiers were used in an effort to

TABLE 47. EMULSION STABILITY OF ETHYLENE/OLEFIN COPOLYMERS

Polymer Trade Name	Emulsifier	Emulsion Stability Break Time, (min)
Petrolite CP-7	Ganex WP-660	5
Trilene CP80	Ganex WP-660	(1)
"	Ganex V-216	(1)
"	Igepon T77	(1)
"	Aerosol TR70	(1)
Eastoflex D139-3	Ganex WP-660	(1)
"	Ganex V-216	(1)
"	Igepon T77	(1)
"	Aerosol TR70	(1)
Eastoflex	Ganex WP-660	(1)
"	Ganex V-216	(1)
"	Igepon T77	(1)
"	Aerosol TR70	(1)
Trilene MB	Ganex WP-660	(1)
Flexomer DEFD 1015	Ganex WP-660	(1)
Vybar 103	Ganex WP-660	5

(1) Too viscous to mix.

reduce the viscosity enough to permit emulsification with the simulant. Only the Vybar 103 and the Petrolite CP-7 gave emulsions and these were rather unstable. In an attempt to reduce viscosity and improve emulsification, blends of the Eastoflex copolymers with triphenyl phosphate in a 1/3 ratio were evaluated. Although the blends were mixable, emulsion stability was poor (only 1 minute) even with Ganex WP-660 surfactant.

(3) Ethylene/Vinyl Acetate Copolymers

Copolymers of ethylene and vinyl acetate have been used in molded explosive formulations with some success (Reference 33). Their properties may be modified by variation in monomer ratio. Table 48 shows properties of the copolymers from DuPont and Allied Signal selected for evaluation.

TABLE 48. PROPERTIES OF COPOLYMERS OF ETHYLENE AND VINYL ACETATE

Weight Percent Vinyl Acetate	Trade Name	MP/(1) Soften. Pt. (°C)	Melt. Index	Est. Sol. Parameter (2)	Tensile Strength (psi)	Elongation (%)
40	Elvax 40W	104	56	9.1	800	1100
25	Elvax 310	88	400	9.0	2000	900

TABLE 48 (continued)

15	Elvax 500	98	2500	8.9	725	90
12	Elvax 660	193	2.5	8.8	3000	800
13	A-C 400	92	--	8.8		

(1) ASTM E-28
(2) $[(\mathrm{cal/cm^3})^{0.5}]$

Except for Elvax 660, the copolymers have softening points in the range that might be acceptable for melt cast systems. Melt indices vary over a wide range. The Brookfield viscosity of the A-C 400 at 140°C is 610 cP; data for lower temperatures are lacking.

The solubility parameter increases with vinyl acetate content; this might aid in the filling of TNT microvoids. Molded explosives containing ethylene/vinyl acetate copolymers have shown decreased impact sensitivity (Reference 34). Also, the copolymers with higher vinyl acetate content provide higher coating efficiency. This should aid desensitization. Better coating and adhesion also improve the mechanical properties of the explosive and allow greater dissipation of impact energy.

The tensile properties of the copolymers indicate that they range from high strength polyethylene plastics to soft, amorphous rubbers with high elongations.

Emulsion stabilities achieved with the ethylene/vinyl acetate copolymers are shown in Table 49.

TABLE 49. EMULSION STABILITY WITH EVA COPOLYMERS AND BLENDS

Polymer	Blending Agent (Ratio)	Emulsifier	Emulsion Stability Break Time (min)
Elvax 40W	--	Ganex WP-660	(1)
"	--	Ganex V-216	(1)
"	--	Ganex V-216 (2)	(1)
"	Kenamide S180 (1/3)	Ganex WP-660	3.5
"	Kenamide S180 (1/3)	Ganex WP-660 (2)	10
Elvax 310	--	Ganex V-216 (2)	(1)
"	Kenamide S180 (1/3)	Ganex WP-660	1
"	Kenamide S180 (1/3)	Ganex WP-660 (2)	0.5
"	Santicizer 148 (1/3)	Ganex WP-660	1
"	Santicizer 148 (1/3)	Ganex WP-660 (2)	1
Elvax 500	--	Ganex WP-660	(1)
"	--	Ganex V-216	(1)
"	--	Ganex V-216 (2)	(1)

TABLE 49 (continued)

"	Kenamide S180 (1/3)	Ganex WP-660 (2)	0.5
"	Kenamide S180 (1/3)	Ganex WP-660	0.5
Elvax 660	--	Ganex WP-660	(1)
"	--	Ganex V-216	(1)
A-C 400	--	Ganex V-216	(1)
"	--	Ganex WP-660	1
"	--	Aerosol TR70	(1)
"	--	Igepon T77	(1)
"	--	Aerosol OT100	(1)
"	Triphenyl Phosphate (1/3)	Ganex WP-660	10

(1) Too viscous to mix.
(2) Emulsifier and wax melted and mixed before adding nitroethane simulant.

The melted copolymers were generally too viscous to incorporate into nitroethane. The least viscous, A-C 400, was tested with a number of emulsifiers but was mixable only with Ganex WP-660 resin. Therefore the copolymers were blended with two of the low molecular weight wax substitutes, Kenamide S 180 and triphenyl phosphate, as well as with Santicizer 148, a common plasticizer. With these blends, emulsification was possible; two were acceptably stable: Kenamide S180/Elvax 660 and triphenyl phosphate/A-C 400.

The blends offer the prospect of desensitization by several mechanisms. The low molecular weight compounds can provide heat absorption, lubricity and microvoid filling, while the polymer can improve the mechanical properties of the explosive. The A-C 400 ethylene/vinyl acetate copolymer shows particular promise in respect to mechanical properties. Also, the blends are expected to coat solid energetic particles better than wax because their components have solubility parameters more closely matching those of the particles.

(4) Ethylene/Acrylic Acid and Ester Copolymers

Copolymers prepared from ethylene and acrylic acid or methyl acrylate were selected to be evaluated since these materials are often used industrially in waxes and as substitutes for waxes. Table 50 shows the properties of several of these copolymers. The A-C and Acyln products are made by Allied Signal and the EMAC resins by Chevron.

TABLE 50. PROPERTIES OF ETHYLENE/ACRYLIC ACID AND ESTER COPOLYMERS

Copolymer	Sol. Parameter (1)	Trade Name	MP Soften. Point (0°C)	Viscosity (cP @ 190°C)	Tensile Strength (psi)	Elongation Est. (%)
Acrylic Acid (Acid No.)						
120	9.0	A-C 5120	102(2)	650	---	---
20	---	Aclyn 285A	82(3)	11000	1350	3
0	---	Aclyn 295A	99(3)	4500	1300	10
Methyl Acrylate (%)						
20	9.0	EMAC 2220	83(3)	4500	1100	780
18	8.9	EMAC 2255	82(3)	15000	1500	680
24	9.0	EMAC SP226	76(3)	---	1390	800

(1) $[(cal/cm^3)^{0.5}]$
(2) ASTM D-3954
(3) DSC

The copolymers have melting points in the proper range for melt-cast application. Their solubility parameters suggest that these materials will fill microvoids and both wet and coat energetic particles better than waxes. Note, however, that the increased parameter for the acrylic acid copolymers may be primarily due to hydrogen bonding forces that are not likely to improve miscibility with TNT.

The copolymers have tensile properties that are expected to improve mechanical properties of the explosive by permitting more deformation and spreading of impact forces. The copolymers of methyl acrylate have lower heat of fusion than polyethylene but higher specific heat. Aclyn 285A and 295A are copolymers of acrylic acid that have been neutralized using sodium and zinc cations, respectively. They have higher heats of fusion than the EMAC polymers but lower than polyethylene.

The emulsion stabilities obtained with these substitutes are shown in Table 51.

TABLE 51. EMULSION STABILITY OF ETHYLENE/ACRYLIC AND ACRYLATE COPOLYMERS

Polymer	Blending Agent (Ratio)	Emulsifier	Emulsion Stability Break Time (min)
A-C 5120	---	Ganex WP-660	1
Aclyn 285A	---	Ganex WP-660	(1)
"	---	Ganex V-216	(1)
"	Kenamide S180 (1/3)	Ganex WP-660	(1)
"	Kenamide S180 (1/3)	Ganex WP-660(2)	0.5
Aclyn 295A	---	Ganex WP-660	(1)
"	---	Ganex V-216	(1)
"	Kenamide S180 (1/3)	Ganex WP-660	0.5
"	Kenamide S180 (1/3)	Ganex WP-660(2)	0.5
"	Santicizer 148 (1/3)	Ganex WP-660	1
"	Santicizer 148 (1/3)	Ganex WP-660 (2)	0.5
EMAC 2220	---	Ganex WP-660	(1)
EMAC 2255	---	Ganex WP-660	(1)
EMAC SP2260	---	Ganex WP-660	(1)

(1) Too viscous to mix
(2) Wax and emulsifier melted and mixed before adding nitroethane

Except for A-C 5120, which gave poor stability, the copolymers were too viscous for mixing at the test temperature. Blends of the ethylene-acrylic copolymers with either Kenamide S180 or Santicizer 148 were mixable but gave unstable emulsions.

(5) Polyethylene Alcohols And Ethoxylates

Polyethylene alcohols are linear polymeric primary alcohols with chain lengths from 24 to 50 carbon atoms. The ethoxylates are prepared by reacting these alcohols with varying amounts of ethylene oxide. Table 52 shows properties of such compounds from Petrolite that were chosen to be evaluated as wax substitutes.

TABLE 52. PROPERTIES OF POLYETHYLENE ALCOHOLS AND ETHOXYLATES

Carbon Chain Length	Ethylene Oxide Content	Trade Name	MP (1) (°C)	Est. Sol. Parameter (2)
32	---	Unilin 425	78	8.7

TABLE 52 (continued)

38	---	Unilin 550	91	8.6
50	---	Unilin 700	99	8.5
32	20	Unithox 420	91	8.5
32	50	Unithox 450	91	8.7
32	80	Unithox 480	86	9.1
38	20	Unithox 520	20	8.5
38	50	Unithox 550	50	8.7

(1) USP XX
(2) $[(\mathrm{cal/cm^3})^{0.5}]$

The selected alcohols and ethoxylates have melting points in the range desired for melt casting. The solubility parameters are slightly higher than that of wax, which suggests better wetting and coating of energetic particles. The specific heats and heats of fusion of these compounds are not available but should be only slightly lower than those of wax. Therefore, quenching of hot spots should be acceptable. Like other waxy materials, the compounds are expected to reduce friction. Mechanical properties of the explosives made with these substitutes should be similar to those of wax-desensitized counterparts.

Table 53 shows the emulsion stability obtained with these compounds using Ganex resin emulsifiers.

TABLE 53. EMULSION STABILITY WITH POLYETHYLENE ALCOHOLS AND ETHOXYLATES

Polymer	Emulsifier	Emulsion Stability Break Time (Min.)
Unilin 425	Ganex V-216	3
"	Ganex WP-660	5
Unilin 550	Ganex V-216	3
"	Ganex WP-660	15
"	Ganex WP-660 (1)	0.5
Unilin 700	Ganex WP-660	10
Unithox 420	Ganex WP-660	10
Unithox 480	Ganex WP-660	10
Unithox 520	Ganex WP-660	10
Unithox 550	Ganex WP-660	45

(1) Wax substitute and emulsifier melted and mixed before nitroethane addition

The stabilities of these emulsions were fairly good; Unilin 550 alcohol and Unithox 550 appear particularly promising. The results obtained using two different methods of emulsion preparation with Unilin 550 illustrate how importantly procedure affects stability.

(6) Acrylate and Methacrylate Polymers

Polymethylmethacrylate polymer has been tested as desensitizer for impact initiation of PETN and was predicted to provide good quenching of hot spots due to its endothermic decomposition at elevated temperatures. However the brittleness of the polymer resulted in less desensitization than expected on the basis of thermal properties alone (Reference 14). Fortunately a variety of nonbrittle acrylate and methacrylate polymers copolymers are available. These may provide the desired thermal quenching. Three polymers from Rohm and Haas shown in Table 54 were chosen for evaluation. Based on melting point, two might be used in melt casting process with little difficulty. Paraloid K120N would have to be somewhat soluble in TNT to serve as a wax substitute.

TABLE 54. PROPERTIES OF ACRYLATE AND METHACRYLATE POLYMERS

Polymer	Trade Name	MP Soften. Pt. (°C)	Specific Heat (cal/g/deg)	Est. Sol. Parameter (1)
Poly(methyl-Methacrylate-ethyl acrylate) Copolymer	Paraloid K120N	132-149	0.34	9.4
Poly(isobutyl-Methacrylate)	Acryloid B67	50	0.36	8.6
Polyacrylate Copolymer	Acryloid DM55	70	---	9.4

(1) $[(cal/cm^3)^{0.5}]$

The softening temperatures shown in the table are those provided by the manufacturer. Melting points of Acryloid B67 and DM55 measured at MACH I were about 20-30 degrees higher.

The solubility parameters of these polymers are closer to those of TNT and other energetic ingredients than those of wax. This implies better filling of microvoids and better coating of particulate solids.

Polymeric wax substitutes as these should be capable of changing the mechanical properties of the explosive, thereby providing another mechanism of desensitization. The literature provides sufficient information on the properties of related polymers to allow estimates of the mechanical properties of these materials (Reference 35). Waxes like Indramic have tensile strengths of 200-400 psi and elastic moduli of 2×10^5 psi indicating brittleness and lack of elasticity (Reference 1). Paraloid K120N is estimated to have tensile strength of 2000-3000 psi and elongation near 10%. Acryloid B67 and DM55 are estimated to have tensile strength of 800-1000 psi with elongation of 200-300%. These properties should yield explosive composites with greater strength and lower modulus, hence greater ability to dissipate shock by bulk deformation (Reference 14).

Table 55 shows stability of emulsions prepared using acrylate and methacrylate polymers.

TABLE 55. EMULSION STABILITY WITH ACRYLATE AND METHACRYLATE POLYMERS

Polymer	Emulsifier	Emulsion Stability Break Time (min)
Acryloid B67	----	>60
"	Ganex WP-660	30
"	Ganex V-216	20
"	Lubrizol OS 87440A	>120
"	Lubrizol OS 22277AJ	15
"	Lubrizol 2633	10
"	Lubrizol OS 47550W	0.5
"	Hi Tech 644	10
"	Hi Tech 646	15
"	Acryloid 956	>120
"	Acryloid 917T	>120
"	Paraloid 106	60
"	LOA 565	>60
Acryloid DM55	Ganex V-216	200
"	Ganex WP-660	3
Paraloid K120N	Ganex V-216	200
"	Ganex V-220	20
"	Ganex WP-660	(1)

(1) Too viscous to mix.

Acryloid B67 gave a clear, stable solution in nitroethane without emulsifier. The solution of polymer also remained stable with addition of a wide variety of emulsifiers. With Ganex V-216 resin emulsifier Acryloid DM55 formed a stable emulsion. Figure 19 shows the appearance at test temperature of Acryloid DM55 (WS 34) and Paraloid K120N (WS 39) with Ganex V-216 resin in nitroethane simulant. Although cloudy, the specimens show good stability. A tube containing Kenamide S with Ganex WP-660 (478) is shown for comparison. Figure 20 shows Acryloid DM55 (WS 34) with Ganex V-216 as a white solid plug and the Paraloid K120N (WS 39) with Ganex V-216 emulsifier as an orange solid at room temperature.

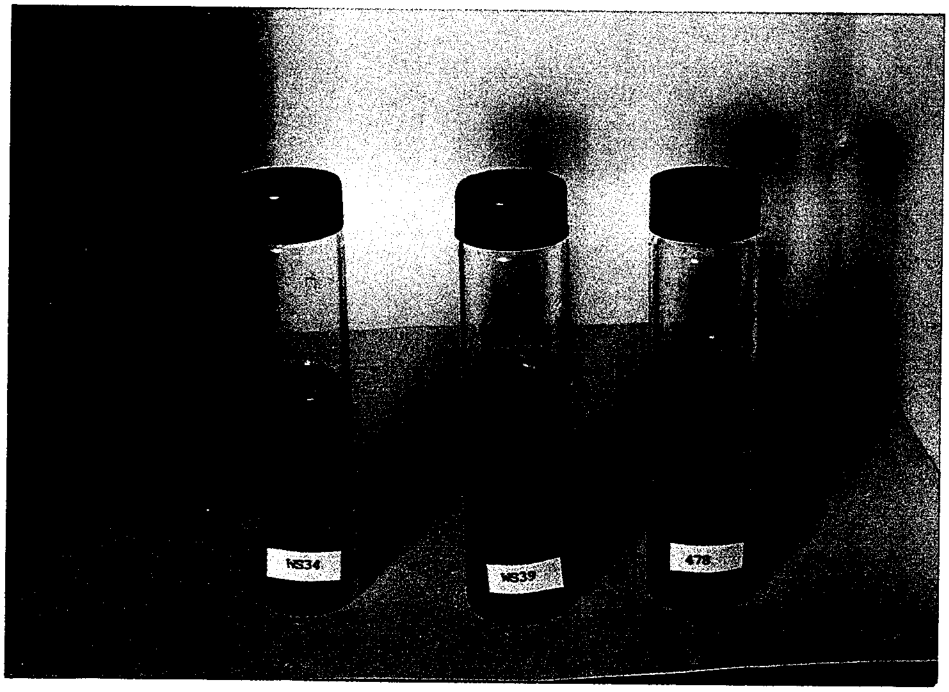


Figure 19. Acryloid DM55 and Paraloid K120N in Nitroethane At Test Temperature

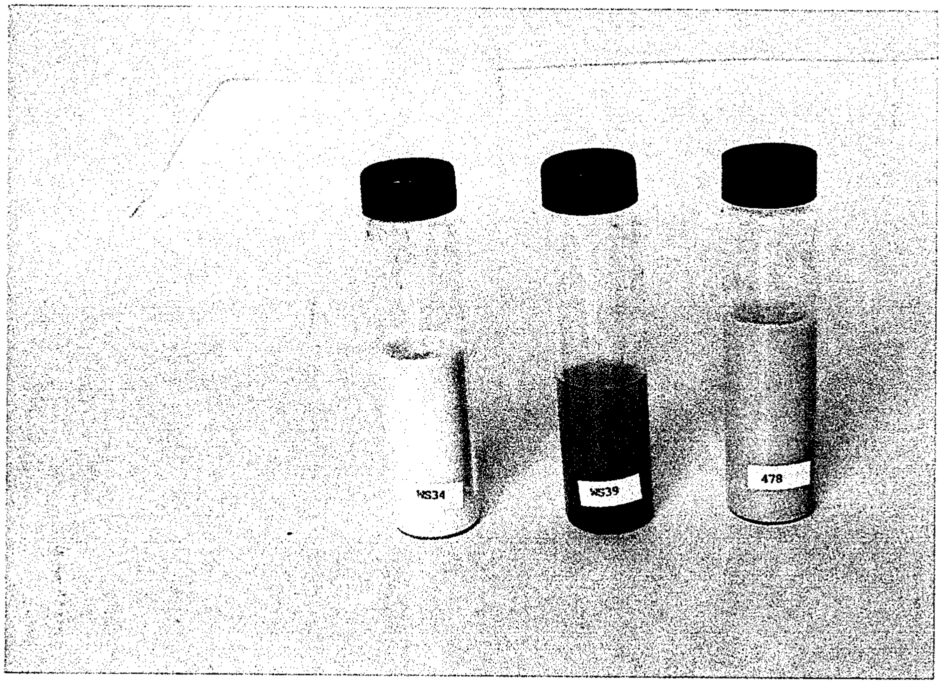


Figure 20. Acryloid DM55 and Paraloid K120N in Nitroethane At Room Temperature

Paraloid K120N has a high melting range, which suggests difficulty in live testing if the polymer is not soluble in TNT. Therefore, several blends of Paraloid K120N were evaluated with other low molecular weight wax substitutes and plasticizers. Test results are shown in Table 56. A 3/1 blend of Kenamide S180 and Paraloid K120N gave a stable emulsion with Ganex WP-660 emulsifier.

TABLE 56. BLENDS OF PARALOID K120N EVALUATED FOR EMULSION STABILITY

Blending Agent (BA)	Ratio (BA/Paraloid)	Emulsifier	Emulsion Stability Break Time (min)
Kenamide S180	3/1	Ganex WP-660	45
Santicizer 148	3/1	Ganex WP-660	0.5
"	3/1	Ganex WP-660(1)	0.5

(1) Wax and emulsifier melted together before adding nitroethane.

(7) Elastomeric-Styrene Block Copolymers

These block copolymers from Shell contain hard styrene blocks combined with soft elastomeric polymeric segments of either butadiene or mono-olefins. The copolymers commonly are added to other materials to increase toughness and dissipate energy, thereby preventing catastrophic failure. If these copolymers could be incorporated into an explosive, a similar mechanism would provide desensitization. Adding 10% of these block copolymers to polyethylene almost doubles impact strength (Reference 36). The structure and properties of two of these block copolymers selected for evaluation are shown in Tables 57 and 58.

TABLE 57. STRUCTURE OF ELASTOMERIC-STYRENE BLOCK COPOLYMERS

Copolymer	Structure	Styrene/Rubber Ratio	Trade Name
Butadiene	Triblock SBS	31/69	Kraton D1101
Ethylene/ butylene	Triblock SEBS	29/71	Kraton G1650

TABLE 58. PROPERTIES OF ELASTOMERIC-STYRENE BLOCK COPOLYMERS

Block Copolymer	Tensile Strength (psi)	Elongation (%)	Hardness Shore A
Kraton D1101	4600	880	71
Kraton G1650	5000	500	---

The block copolymers behave as if they had two distinct solid phases. Each phase consists of a block of the copolymer with its own solubility parameter. The styrene block has a solubility parameter of 9.1 while that of the butadiene midblock is about 8.4. The solubility parameter of the ethylene/butylene midblock is 7.9 (Reference 36).

As shown in Table 59, the high viscosity of the block copolymers precluded formation of emulsions. Many emulsifiers were tested, but none solved the problem. However, blending the block copolymers with less viscous wax substitutes and plasticizers overcame the viscosity problem. Results shown in Table 60 indicate that the 1/1 blend of Santicizer

TABLE 59. EMULSION STABILITY OF ELASTOMERIC-STYRENE BLOCK COPOLYMERS

Copolymer	Emulsifier	Emulsion Stability Break Time (min)
Kraton D1101	Ganex V-216	(1)
"	Ganex WP-660	(1)
"	Paraloid 106	(1)
"	Acryloid 917T	(1)
"	Acryloid 956	(1)
"	Hi Tech 644	(1)
"	Hi Tech 646	(1)
"	LOA 565	(1)
"	Lubrizol 2631	(1)
"	Lubrizol 2633	(1)
"	Lubrizol OS 47550W	(1)
"	Lubrizol OS 22277AJ	(1)
"	Lubrizol OS 87440A	(1)
Kraton G1650	Ganex V-216	(1)

(1) Too viscous to mix.

TABLE 60. EMULSION STABILITY OF KRATON BLOCK COPOLYMER BLENDS

Blending Agent(BA)	Kraton Copolymer	Ratio (BA/KRATON)	Emulsifier	Emulsion Stability Break Time (min)
Kenamide S180	D1101	3/1	Ganex WP-660	0.5
"	G1650	3/1	"	0.5
Kenamide S	D1101	3/1	---	5
"	D1101	3/1	Ganex WP-660	5
Santicizer 148	D1101	1/1	"	30
"	D1101	3/1	"	0.5
"	G1650	3/1	"	0.5
Triphenyl Phosphate	D1101	3/1	"	1

148 and Kraton D1101 provided a system with good emulsion stability.

Much lower levels of Kraton D1101 were then substituted for part of the Ganex emulsifier. Kraton levels of 20, 30 and 40% of total emulsifier with Ganex WP-660, V-220 or V-216 emulsifier, gave emulsion stability with wax substitute Kenamide S of 180 to 210 minutes as shown in Table 61. These Kraton levels amount to 4, 6 and 8% of the wax substitute. The Kraton creates a gel structure with increased tensile strength and flexibility. The same level of Kraton as a percent of the wax substitute but without any Ganex emulsifier gives stability that is satisfactory, but far less than that obtained with any of the three Ganex resin surfactants.

Without Ganex resin emulsifier, Kenamide S180 containing 2 and 4% Kraton D1101 gave 15 and 10 minutes stability, respectively. Ganex WP-660 resin impaired stability of the Kraton D1101/Kenamide S180 mixes.

TABLE 61. EMULSION STABILITY OF KRATON BLOCK COPOLYMER BLENDS

Emulsifier Ganex No.	Ratio Ganex to Kraton D1101	Kraton % of WS	Wax Substitute (WS)	Emulsion Stability Break Time, min(1)
WP-660	90/10	2	Kenamide S	>30
"	80/20	4	"	180(2)
"	70/30	6	"	180(2)
"	60/40	8	"	210(3)
None		2	"	10
"		4	"	10
"		6	"	10
V-220	80/20	4	"	210(3)

TABLE 61 (continued)

"	70/30	6	"	210(3)
"	60/40	8	"	210(3)
V-216	80/20	4	"	210(3)
"	70/30	6	"	210(3)
"	60/40	8	"	210(3)
None		2	Kenamide S180	15
"		4	"	10
"		6	"	3
WP-660	90/10	2	"	3
"	80/30	4	"	1
"	70/30	6	"	1
"	90/10	2	Triphenylphosphate	0.5
"	80/20	4	"	0.5
"	70/30	6	"	0.5

(1) In nitroethane.
(2) Became hazy at 60 minutes.
(3) Clear the whole time.

(8) Acrylonitrile Copolymers

Zeon supplies acrylonitrile copolymers that might improve the mechanical properties of an explosive. Having high solubility parameters (i.e., closer to that of TNT), they also should be miscible and effectively wet and coat energetic particles. Table 62 shows the structures and properties of three of these copolymers which were chosen for evaluation. Two of these copolymers are liquid at room temperature.

TABLE 62. SELECTED PROPERTIES OF ACRYLONITRILE COPOLYMERS

Copolymer (Wt.%) Parameter	Trade Name	MP Soften. Pt. (°C)	Viscosity (cP @ 90°C)	Est. Specific Heat (cal/g/°C)	Est. Sol. (1) Parameter
Butadiene (72)	Nipol 1312	-39	2000	0.42	10.1
Butadiene (74)	Nipol 1312LV	-45	1500	0.42	10.1
Hydrogenated Butadiene (64)	Zetpol 2000	---	---	0.4	9.9

(1) [$(\text{cal/cm}^3)^{0.5}$]

The third, higher molecular weight copolymer is hydrogenated to improve aging stability.

The emulsion stabilities obtained with these copolymers are shown in Table 63. The lower molecular weight, liquid copolymers form stable solutions in nitroethane at the test temperature. Addition of Ganex emulsifiers did not affect stability. The higher molecular weight Zetpol copolymer was too viscous for testing alone. Blends with a lower molecular weight copolymer did not give stability.

TABLE 63. EMULSION STABILITY OF ACRYLONITRILE COPOLYMERS

Copolymer	Emulsifier	Emulsion Stability Break Time (min)
Nipol 1312	---	60
	Ganex WP-660	>90
Nipol 1312LV	---	
	Ganex WP-660	>90
Zetpol 2000	Ganex V-216	(1)
Nipol 1312LV Zetpol 2000 (3/1)	Ganex V-216	0.5

(1) Too viscous to mix.

4. WAX SUBSTITUTE CANDIDATE DESENSITIZERS WITH EMULSIFIERS

The following chemicals, polymers and blends have shown acceptable emulsion stability and, on the basis of their physical properties, may excel wax as a desensitizer:

Compound or Blend	Tradename
Stearamide	Kenamide S
Stearyl stearamide	Kenamide S180
Erucamide	Kenamide E
Erucyl stearamide	Kenamide S221
Propylene carbonate	Arconate
Triphenyl phosphate	TPP
Naphthenic process oil	Telura 343
Polyacrylate copolymer	Acryloid DM55
Polyisobutylmethacrylate	Acryloid B67
Ethoxylated polyethylene	Unithox 550
Hydroxyhexylamine alkylbenzene sulfonate	Ultrawet 101

Butadiene/acrylonitrile copolymer	Nipol 1312
Methyl methacrylate/ethyl acrylate copolymer	Paraloid K120N
Blend of stearyl stearamide	Kenamide S180
and butadiene/styrene block copolymer	Kraton D1101
Blend of isodecyldiphenylphosphate	Santicizer 148
and butadiene/styrene block copolymer	Kraton D1101
Blend of triphenyl phosphate	TPP
and ethylene/vinyl acetate copolymer	A-C 400A

For each of these wax substitutes, an emulsifier has been identified that provides acceptable emulsion stability or may be used to achieve other benefits without degrading emulsion stability.

5. EXPLOSIVE TESTING AT WL/MNME

The above wax substitutes, which passed tests for emulsion stability with the nitroethane simulant at MACH I, were tested in live mixes with TNT at WL/MNME. The chemical compatibility with TNT was determined by DSC of milligram-size samples and recording the change in the TNT exotherm. Test results are shown in Table 64.

TABLE 64. COMPATIBILITY OF WAX SUBSTITUTE CANDIDATES WITH TNT

Name	State	Composition	Exotherm with TNT (°C)
TNT	______	(Control)	300
Kenamide E	Solid	Erucamide	250
Kenamide S180	Solid	Stearyl stearamide	281
Kenamide S221	Solid	Erucyl stearamide	265
Kenamide S	Solid	Stearamide	280
Arconate	Liquid	Propylene carbonate	268
TPP	Solid	Triphenyl phosphate	312
Telura 343	Liquid	Naphthenic process oil	272
Acryloid DM55	Solid	Polyacrylate	281
Acryloid B67	Solid	Polyacrylate	295
Paraloid K120N	Solid	Methyl methacrylate	297
Unithox 550	Solid	Ethoxylated polyethylene	271
Ultrawet A101	Liquid	Hydroxyhexylamine-alkyl-benzene sulfonate	170
Nipol 1312	Liquid	Butadiene-Acrylonitrile	260
Nipol 1312lv	Liquid	Butadiene-Acrylonitrile	258
Kraton D1101	Solid	Butadiene-Styrene Block	244
Santicizer 148	Liquid	Isodecyl diphenyl phosphate	289
A-C 400	Solid	Ethylene-vinyl acetate	285

The results show that triphenyl phosphate actually increases the thermal stability of TNT. In contrast, Ultrawet A101, markedly depresses the exotherm and is clearly incompatible with TNT. The remaining candidates are considered to be acceptably compatible with TNT.

Miscibility was tested at WL/MNME by melting a 3 gram sample of TNT and adding a 1 gram sample of the wax substitute at 95°C. The mixture was stirred, allowed to stand and observed at 5 minute intervals to note whether and when separation occurred. Eight to 24 mg of Ganex WP-660 was then added to each immiscible sample and stirring was repeated. Separation was again noted at 5 minute intervals. The results obtained are shown in the Tables 65 and 66.

TABLE 65. MISCIBILITY OF WAX SUBSTITUTE CANDIDATES WITH MOLTEN TNT

Candidate	With TNT	Added(1) Ganex WP-660	Casting	Comments
Kenamide E	Emulsion	Some help	Tan	Slow stratification
Kenamide S180	Insoluble	Stable	Tan	Toffee colored emulsion
Kenamide S221	Insoluble	Helps	Red-purple	Unstable emulsion
Kenamide S	Suspended	Helps(2)	Tan	Fairly homogeneous
Arconate	Soluble	---	Yellow	Casting not cohesive
TPP	Soluble	---	Yellow	Tends to supercool
Telura 343	Insoluble	Fairly Stable	Orange	Slight separation over 30 min
Acryloid DM55	Insoluble	Some help	Reddish	Solid did not all dissolve
Acryloid B67	Insoluble	Some help	Reddish	Solid did not all dissolve
Paraloid K120N	Gooey mass	Gooey mass	Purple Brittle	Extrudable
Unithox 550	Insoluble	No help	Red-orange	Separated <5 Min.
Nipol 1312	Emulsion	---	Yellow	Stable emulsion

TABLE 65 (continued)

Nipol 1312lv	Emulsion	---	Yellow Sticky	Some settling
Kraton D1101	Insoluble	No effect	Brown	Solid did not all dissolve
Santicizer 148	Soluble	---	Yellow	Casting dissolved tray
A-C 400	Insoluble	Unstable	Tan	Separates <1 min.

(1) 0.8 to 2.4% Ganex WP-660 added based on wax. Composition D-2 and all simulant emulsion stability tests use approximately 20% emulsifier based on wax.
(2) Ganex V-216 and Ganex WP-660 both help.

TABLE 66. MISCIBILITY OF WAX SUBSTITUTE BLENDS WITH MOLTEN TNT

Blend	Ratio	With TNT	With Ganex	Casting	Comments
Kenamide S180 Kraton D1101	3/1	Insoluble	Some	Red-yellow	Kraton layer red
Santicizer 148 Kraton D1101	1/1	Insoluble	Much	Tan	Kraton floats to top
TPP A-C 400	3/1	Soluble	---	Yellow	Soft pliable casting

TPP, Arconate, Santicizer 148 and the TPP/A-C 400 blend are all miscible with TNT. Kenamide S180 with Ganex WP-660 resin and the Nipols formed the best emulsions. Telura 343, Kenamide E, the Santicizer 148/Kraton D1101 blend, and Kenamide S, all with Ganex WP-660 resin emulsifier are next best. The remaining candidates did not provide acceptable systems under the conditions tested (i.e., with only 0.8-2.4% Ganex WP-660 resin based on wax).

With 20% Ganex WP-660 resin, corresponding to Composition D-2 and the simulant test levels, all of the results probably would have been acceptable. Thus many of the rejected candidates might perform well in optimized formulations. Because the various desensitizers can be expected to operate by different means, important practical benefits might well be gained by further study of rejected candidates.

Eleven wax substitutes passed these preliminary tests and are ready for the regimen of safety and performance tests employed to qualify operational explosives. The technical objective of Task 4, to identify wax substitutes that should be good desensitizers, has been achieved. The contractual requirement of four substitutes has been exceeded. Sixteen candidates were submitted, and at least eleven of these are immediately suitable for continued R&D at WL/MNME.

6. COSTS

Current prices of the candidate wax substitutes are shown in Table 67. The polar desensitizers cost $0.46 to $3.29/lb. in truck load quantity. Most cost more than the synthetic polyethylene Polywax 600 wax ($1.19/lb.) and the microcrystalline petroleum wax Indramic 800 ($0.90/lb). The naphthenic process oil Telura 343 costs only $1.50/gal.

TABLE 67. PRICES OF WAX SUBSTITUTES

Product Name	Manufacturer	Price $/lb Truckload
A-C 400 Copolymer	Allied-Signal Inc.	1.35 delivd
A-C 400A Copolymer	Allied-Signal Inc.	1.38 delivd
Kenamide S	Witco Chemical Co.	1.51 FOB
Kenamide S180	Witco Chemical Co.	2.45 FOB
Kenamide S221	Witco Chemical Co.	3.29 FOB
Kenamide E	Witco Chemical Co.	2.85 FOB
Triphenylphosphate	Monsanto Company	1.89 frt all
Santicizer 148	Monsanto Company	1.64 frt all
Nipol 1312	Zeon Chemicals Co.	1.56 FOB
Nipol 1312 lv	Zeon Chemicals Co.	1.56 FOB
Arconate	Arco Chemical Co.	0.46 FOB
Kraton D1101	Shell Chemical Co.	1.05 FOB
Telura 343	Exxon Company USA	1.50/gal(1) FOB
Reference:		
Polywax 600	Petrolite Corp.	1.19 FOB
Polywax 500	Petrolite Corp.	1.1825 FOB
Indramic 800	Industrial Raw Materials Corp.	0.895 FOB
Indramic 170C	Industrial Raw Materials Corp.	0.75 FOB

(1) Tank wagon

The generally higher cost of the polar desensitizers may well be justified by many potential improvements in processability and performance discussed elsewhere in this report.

7. CONCLUSIONS

All objectives of Task 4 have been met or exceeded.

A minimum of four wax substitutes with expected desensitizing properties was to be submitted to WL/MNME for live evaluation. Sixteen, including blends, were submitted.

At least one emulsifier providing good emulsion stability with nitroethane TNT simulant has been identified for each wax substitute. In many cases either of two Ganex emulsifiers was effective.

At least one substitute was to be a better desensitizer than wax. MACH I selected the substitutes to exploit various mechanisms of desensitization. It is reasonable to expect that several substitutes in blends, if not alone, will outperform wax.

A polar liquid or low melting point desensitizer may be more effective than wax because it will lower the mix viscosity and thereby improve wetting, coating and dispersion of the explosive fillers. All these processes not only promote desensitization but also increase production rate by shortening mix and casting times. Alternatively, lowered viscosity may be traded for higher solids loading.

Polar desensitizers may be less subject to exudation than wax because they are more likely to dissolve in TNT or bond to explosive fillers.

Polar desensitizers with melting points near that of microcrystalline wax (e.g., Indramic 800) are expected to coat explosive fillers more easily and completely than wax. This is one of the more important mechanisms in desensitization.

Phosphate esters are established fire retardants. Their effectiveness in desensitization will have to be determined.

Optimum desensitization depends on how the explosive is used. For example, the shocks imposed on shells and bombs differ in both intensity and duration. Different desensitizers for differing applications may be desirable.

If a desensitized composition suffers from diminished explosive yield or insensitivity to the fuze, the condition may be correctable by replacing the desensitizer with a substitute that operates by a different mechanism. The substitute might be used alone or blended with wax.

Wax substitutes offer much greater flexibility than natural or synthetic hydrocarbon waxes. They are synthetic chemicals available in good quantity. In contrast to petroleum waxes, their quality is good and properties are consistent over many years.

Generally the substitutes are much easier to emulsify in TNT and NE than microcrystalline petroleum wax. Polywax 600, an unbranched synthetic polyethylene wax is difficult to emulsify with NE, 2,4-DNT or TNT because of its lack of branching. The polar wax substitutes are far better choices for flexibility.

Limitation of time and resources precluded optimization of desensitzer systems for emulsion stability. Any desensitizer of interest that exhibited poor emulsion stability should receive further study.

The polar desensitizers cost $0.46 to $3.29/lb in truck load quantity. Most cost more than the synthetic polyethylene Polywax 600 ($1.19/lb) and the microcrystalline petroleum wax Indramic 800 ($0.90/lb). The naphthenic process oil Telura 343 costs only $1.50/gal. The higher cost of the polar desensitizers may be justified by important potential improvements in performance.

SECTION VII

EVALUATION OF SURFACTANTS FOR MICROCRYSTALLINE WAX AND POLYWAX 600 SYNTHETIC POLYETHYLENE WAX

1. SUMMARY

An objective of Task 4 is to develop an emulsifier that will provide satisfactory emulsion stability for synthetic polyethylene wax Polywax 600 in nitroethane simulant for TNT. This has been accomplished.

Another objective is to develop a good emulsifier for Indramic 170C microcrystalline wax that differs in chemical structure from the Ganex resin family. The intent is to identify a back-up emulsifier. This has not been accomplished. Evidently the effectiveness of the Ganex resin family is unique.

In the course of developing emulsifiers for many different waxes and wax substitutes, it was desirable to develop emulsion stability patterns for various emulsifier families. More than 200 surfactants and blends were evaluated in Phase I of this program, but only the Ganex resin series gave acceptable emulsion stability with the waxes and nitroethane simulant. Since the nitrogen in Ganex resin additives was suspected of being responsible for their effectiveness, the following classes of nitrogen-containing emulsifiers were investigated:

- Amine salts of:
    - Sulfonic acids
    - Carboxylic acids
    - Organic phosphoric acid partial esters
- Other nitrogen containing surfactants:
    - Pyrollidones
    - Succinimides
    - Taurates
    - Sarcosines.

Many novel amine salts and esters were synthesized for this evaluation.

A number of other approaches were evaluated in search of the emulsifier or co-emulsifier. These included:

- Coupling agents
- Plasticizers
- Solvents
- HLB selection
- Solubility parameter selection.

A good emulsifier for Polywax 600 was finally found. Ganex WP-660 alone gave only 3 minutes emulsion stability with nitroethane simulant. However, by blending 10-15% of a styrene/butadiene block copolymer (Kraton D1101) with the Ganex WP-660, the stability was increased to 10 minutes, a completely satisfactory level. Thus the objective of developing an emulsifier for Polywax 600 has been achieved. The emulsifier blend has been evaluated by WL/MNME for miscibility (emulsion stability) with TNT. Gratifying stability times of 10 to 20 minutes were obtained in three tests.

An exhaustive search for an emulsifier of different chemical structure than Ganex resins for microcrystalline Indramic wax has been unsuccessful. This demonstrates the clear superiority of Ganex WP-660, which provides a number of other valuable benefits including:

- Increased wetting of particles
- Better dispersion of particles
- Greater reduction of friction
- Greater reduction of viscosity
- Increased density by reduction of trapped air
- Filling of voids
- Greater desensitization
- Increased production rate for TNT melt casting and PBX processing
- Higher attainable solids loading.

Optical photomicrographs have been taken of a number of emulsions of wax in simulant (NE and 2,4-DNT) with and without Ganex emulsifier. The photomicrographs confirm the stated benefits of Ganex in respect to wetting, coating, and dispersion of wax on 2,4-DNT crystals or emulsified droplets in nitroethane or molten 2,4-DNT.

SEM photomicrographs show that 2.3% Ganex WP-660 in a 75% TNT and 22.7% wax composition explosive casting greatly reduced brittleness as evidenced by fracture lines created in sectioning the casting for SEM when compared to a 75% TNT and a 25% Composition D-2 explosive containing 4.0% nitrocellulose plus lecithin. Composition D-2 consists of 84% wax, 14% nitrocellulose and 2% lecithin. This verifies the very valuable ancillary benefits of the Ganex resin emulsifiers.

SEM photomicrographs of wax emulsified with 0.1% Ganex WP-660 in an aluminized Octol (HMX/TNT) explosive casting showed better coating of HMX crystals, stronger HMX crystals, and better void filling than the same composition emulsified with 0.3% lecithin. To the unaided eye the Ganex WP-660 casting appeared better than the lecithin counterpart. This further confirms the cited benefits in an explosive composition.

2. INTRODUCTION

In Phase I, Mach I identified a group of alkyl polyvinylpyrrolidone resin surfactants that proved to be excellent emulsifiers, verified the results, and submitted samples to WL/MNME. Here they were evaluated and their effectiveness verified by emulsifying molten TNT and Indramic 170C wax. These emulsifiers are made and sold by International Specialty Products Company (formerly GAF) under the trade name Ganex resins.

The alkyl polyvinylpyrrolidone resins (Ganex surfactants) were selected for evaluation because they contain a repeating cyclic amide structure along the polymer chain that was expected to provide compatibility with nitroethane and TNT. Ganex surfactants are used commercially as dispersants in anhydrous cosmetics, suggesting compatibility with the wax present in some of these compositions. A review of Ganex resin technical literature then showed that Ganex V-220 is insoluble in nitromethane and nitropropane and partially soluble in nitroethane. It is also soluble in mineral oil. These properties appeared very promising. Structural variations in the three Ganex resin products appeared to offer good flexibility for adjustment of compatibility, emulsion stability, dispersancy and other properties as needed. Properties, structures and uses of the Ganex resin products are shown in Appendix A.

3. RESULTS

a. Ganex Resin Emulsifiers, Salts and Blends

The Ganex resin emulsifiers are alkyl polyvinylpyrrolidones (PVP) in which the alkyl group differentiates the three products. Table 68 shows structural characteristics of each product. Appendix A provides a more detailed description of the surfactants, their structure and their uses.

TABLE 68. GANEX EMULSIFIERS

Name	Alkyl Group		% Nitrogen	Molecular Weight
	Carbon No.	No. Per (PVP)		
Ganex V-216	16	2	2.0-3.0	7300
Ganex V-220	20	1	2.9-3.6	8600
Ganex WP-660	30	1	2.0-3.0	5000

The Ganex resin emulsifiers, especially V-216 and WP-660, provide acceptable emulsion stability with Indramic waxes and the simulants. The emulsifiers were tested by WL/MNME and found to provide acceptable emulsion stability with TNT and the microcrystalline petroleum waxes they evaluated. Emulsion stability results obtained by MACH I with simulants for TNT are compared in the Table 69.

TABLE 69. EMULSION STABILITY OF INDRAMIC 170C WAX USING GANEX EMULSIFIERS

Emulsifier	Wax	Simulant	Emulsion Stability Break Time(Min.)
Ganex V-216	Indramic 170C	Nitroethane	1
"	"	2,4-DNT	30
Ganex V-220	"	Nitroethane	5
"	"	2,4-DNT	3
Ganex WP-660	"	Nitroethane	15
"	"	2,4-DNT	30
Ganex V-216	Polywax 600	Nitroethane	1
"	"	2,4-DNT	0.5
Ganex V-220	"	Nitroethane	1
"	"	2,4-DNT	0.5
Ganex WP-660	"	Nitroethane	3
"	"	2,4-DNT	3

The results show that in Indramic 170C wax Ganex WP-660 gives good stability with either of the simulants while Ganex V-220 provides only marginal stability. Ganex V-216 gave good stability with Indramic 170C wax in 2,4-DNT but poor stability in nitroethane. Initial testing at WL/MNME of Indramic wax with V-216 in TNT indicated poor stability; this correlated with the results using nitroethane simulant. However, subsequent testing at WL/MNME showed good stability for the V-216 in TNT and led MACH I to switch to 2,4-DNT simulant for better correlation with the live explosive results. Using Polywax 600, lower stability was found with all of the Ganex resin emulsifiers in both simulants.

Surface tensions of the components of the stable emulsion systems were measured to determine the effect of the emulsifiers on the system and gain insight into the nature of the surfaces formed by the Ganex emulsifiers. At surfactant concentrations above the critical level required for micelle formation in a solution of water and nonionic surfactant, the surface is a close-packed array of molecules of the surface active agent. As a first approximation, one can disregard water molecules that are several angstroms distant from the surface. Consequently the surface tension of the solution is very close to that of the pure liquid nonionic surfactant (Reference 37).

Surface tension measurements were made using the capillary rise method. The capillary tube diameter was determined by calibration using distilled water at room temperature. Measurements of the Ganex additive, waxes and simulants were made at 100-103 °C in an oven. Densities of the components were also determined at this temperature. Due to variations in oven temperature caused by taking measurements, the values obtained are not precise(±3 dynes/cm). However, as shown in Tables 70 and 71, they suffice to reveal the effects of the emulsifiers on the various components.

TABLE 70. SURFACE TENSION MEASUREMENTS ON PURE COMPONENTS AT 100-103 °C.

Chemical	Density (g/cm^3)	Surface Tension (dynes/cm)
Ganex WP-660	0.83	52.4
Ganex V-216	0.70	20.6
2,4-DNT	1.25	41.1
Indramic 170C	0.76	24.9
Polywax 600	0.76	26.8

TABLE 71. SURFACE TENSION OF MIXTURES OF EMULSIFIER AND COMPONENTS AT 100-103 °C.

Chemical	Emulsifier	Conc. (wt %)	Surface Tension (dynes/cm)
2,4-DNT	Ganex WP-660	2	34.5
"	"	4	35.3
"	"	6	32.3
"	"	8	28.2
2,4-DNT	Ganex V-216	2	24.7
"	"	4	23.6
"	"	6	22.5
"	"	8	19.9
Indramic 170C	Ganex WP-660	6	25.1
Polywax 600	Ganex WP-660	6	25.5

These data show that both emulsifiers lower the surface tension of the simulant and indicate that the emulsifier does migrate to the interface and create micelles in the 2,4-DNT. Clearly the two emulsifiers do not operate identically. The V-216 appears to lower surface tension by a mechanism similar to that postulated for aqueous/nonionic systems by forming a surface on the solution that is packed with Ganex V-216 molecules. Ganex WP-660, however appears to operate differently, having a very high surface tension itself but lowering the surface tension of the 2,4-DNT when dissolved in it. Obviously the surface of the solution of the Ganex WP-660 in 2,4-DNT is much different from the surfaces of either of the pure components, possibly being a mixture of the two chemicals packed together in a unique array.

The mixture of Ganex WP-660 with either wax has surface tension very close to that of the pure wax.

The stability that Ganex resin emulsifiers confer on the mixture at the test temperature persists on cooling to room temperature. Figure 21 shows the results of three stability tests. Tube 1092 contains Ganex WP-660 with Indramic 170C wax in nitroethane simulant. Tubes 575 and 976 contain emulsifiers that failed to give good emulsion stability. The Ganex resin-containing mixture produced a uniform solid gel while the other emulsifiers permitted distinct separation of the components. The unsuccessful emulsifiers are Silwet L7500 and a Pluronic blend, respectively.

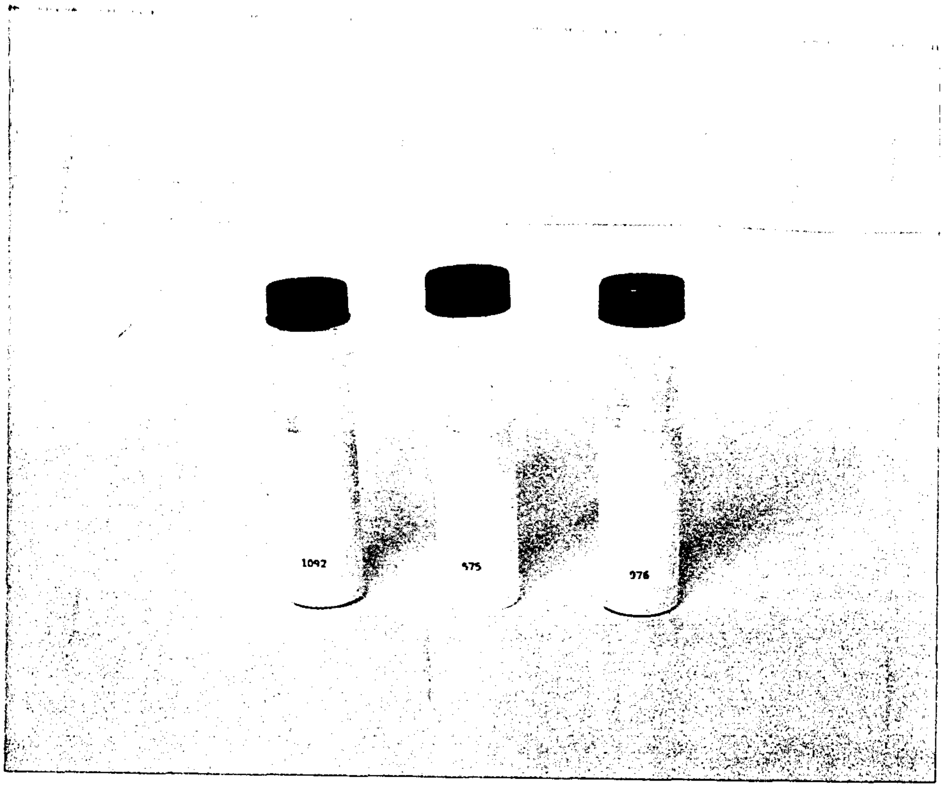


Figure 21. Nitroethane and Indramic 170C Wax Using Ganex WP-660, Silwet L7500, Pluronic Blend Emulsifiers At Room Temperature

The following optical photomicrographs of Ganex resin emulsifiers in the various components of the emulsion system illustrate how the emulsifiers provide good emulsion stability and wax dipersability in the simulants. The first series shows that Ganex V-216 does not provide stable emulsions or good wax dispersion with nitroethane simulant. Figure 22 shows the dispersion of Ganex V-216 in nitroethane as small droplets at room temperature; Ganex V-216 is only partially soluble. The same is true even at the standard test temperature.

Figure 23 shows the structure of a mixture of Ganex V-216, Indramic 170C wax, and nitroethane that was mixed at test temperature and then cooled to room temperature. The Ganex V-216 is dispersed as a liquid in rather large drops with nitroethane in a background of the wax-nitroethane. The wax exhibits a crystalline structure.

Inspection at higher magnification of one of the drops seen in Figure 22 reveals Brownian movement of very small, floating wax crystals (Figure 24). This indicates a predominantly liquid structure.

Figures 25 and 26 show two magnifications of Ganex WP-660 with Indramic 170C wax in nitroethane at room temperature. This combination yields a stable emulsion at test temperature and a uniform white solid when cooled to room temperature. The photomicrographs show the generally uniform structure of the mixture to be mainly a microcrystalline wax/nitroethane gel.

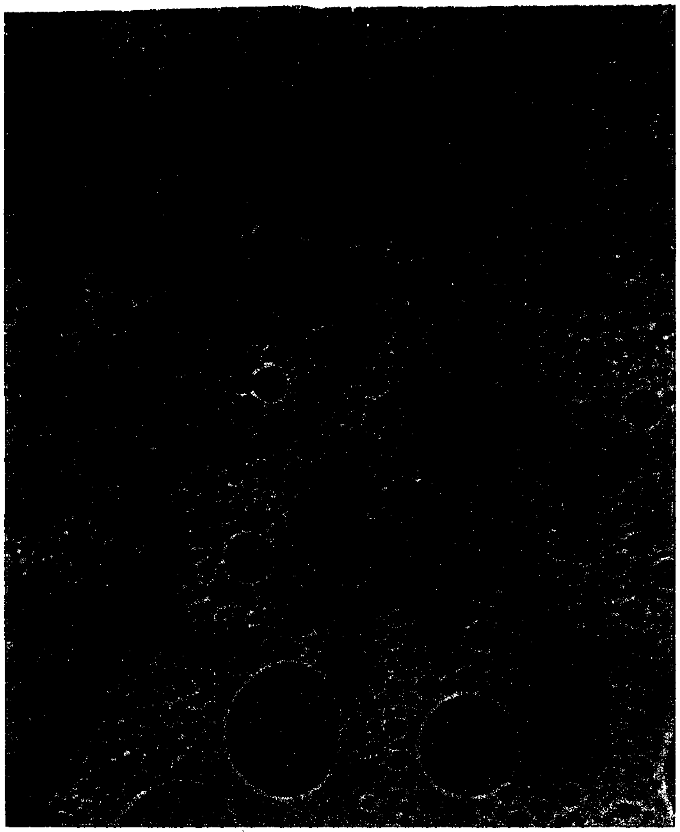


Figure 22. Ganex V-216 In Nitroethane At Room Temperature (100X)

Figure 23. Ganex V-216 With Indramic 170C Wax In Nitroethane At Room Temperature (100X)

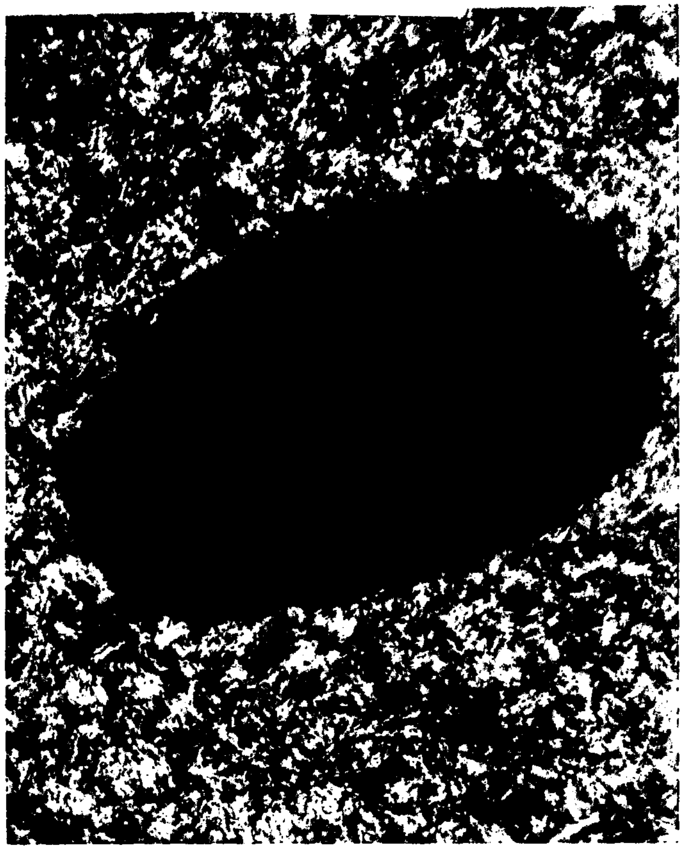


Figure 24. Magnification Of Ganex V-216-Nitroethane Droplet In Wax-Nitroethane (400X)

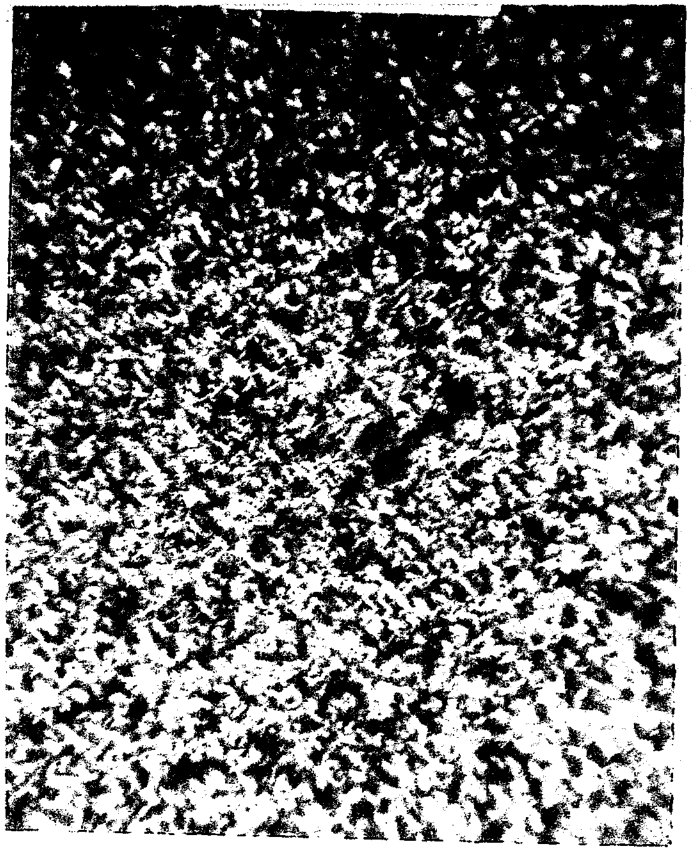


Figure 25. Ganex WP-660 With Indramic 170C WAx And Nitroethane Simulant (100X)

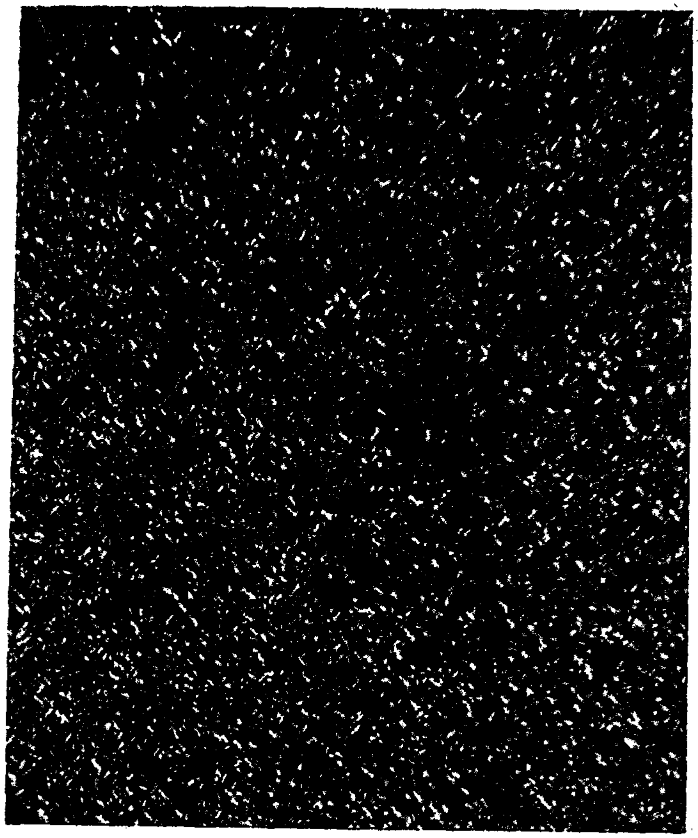


Figure 26. Ganex WP-660 With Indramic 170C Wax And Nitroethane Simulant (400X)

An occasional irregularity appears in the uniform structure as shown in Figure 27. The photomicrograph reveals that this anomaly consists of a mass of very fine spheres. The cluster may be a counterpart to the Ganex V-216/nitroethane droplets shown above, but since Ganex WP-660 is a much better emulsifier in this system, the droplets are much smaller.

Figure 27. Ganex WP-660 Droplet Mass In Microcrystaline Wax-Nitroethane Gel (400X)

Figure 28 shows Ganex WP-660 resin emulsifier with Polywax 600 and nitroethane. At the test temperature this system is less stable (3 min.) than Ganex WP-660 with Indramic 170C wax (15 min.) but more stable than Ganex V-216/Indramic 170C wax (1 min.).

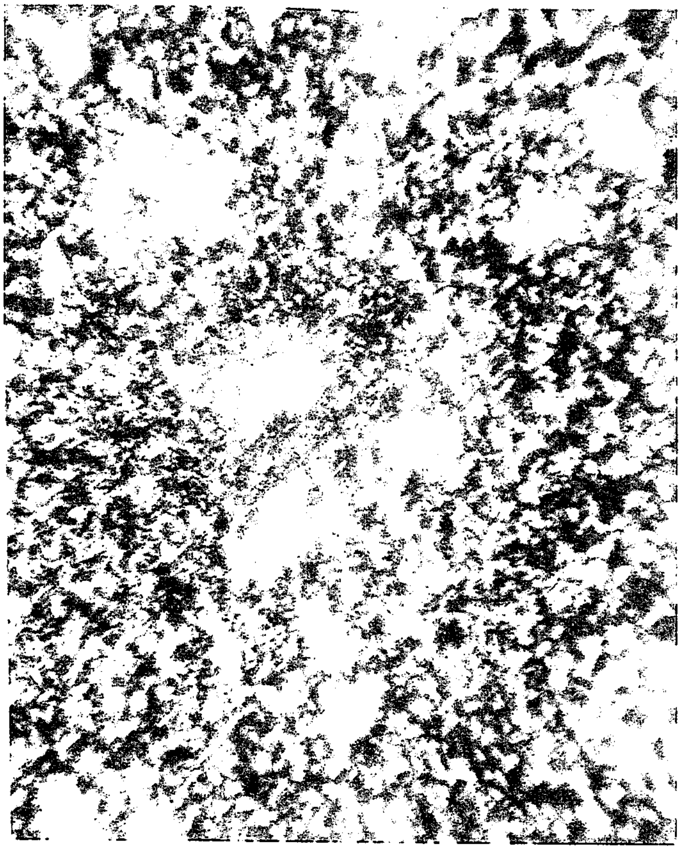


Figure 28. Ganex WP-660 With Polywax 600 In Nitroethane (100X)

The structure here is not as uniform as that of Ganex WP-660/Indramic 170C wax; many more of the masses of small spherical droplets are present. Magnification (Figure 29) shows that their structure is similar to that of the less numerous masses in Ganex WP-660/Indramic 170C.

Figure 29. Ganex WP-660/Nitroethane Droplets in Polywax 600/Nitroethane Gel (400X).

Since both of these systems were sampled shortly after shaking at test temperature, it appears that the masses of droplets arise when the dispersed system begins to coalesce. Because the lifetime of the emulsion of Ganex WP-660/Polywax 600 is shorter, more of these droplet masses form as the emulsion ages.

The use of the 2,4-DNT simulant with these two waxes gives a better indication of the manner in which the wax is dispersed and allows photomicrography at elevated temperatures. Figures 30-32 show the structure of 2,4-DNT simulant at room temperature.

Figure 30. 2,4-DNT Simulant At Room Temperature (100X In Color)

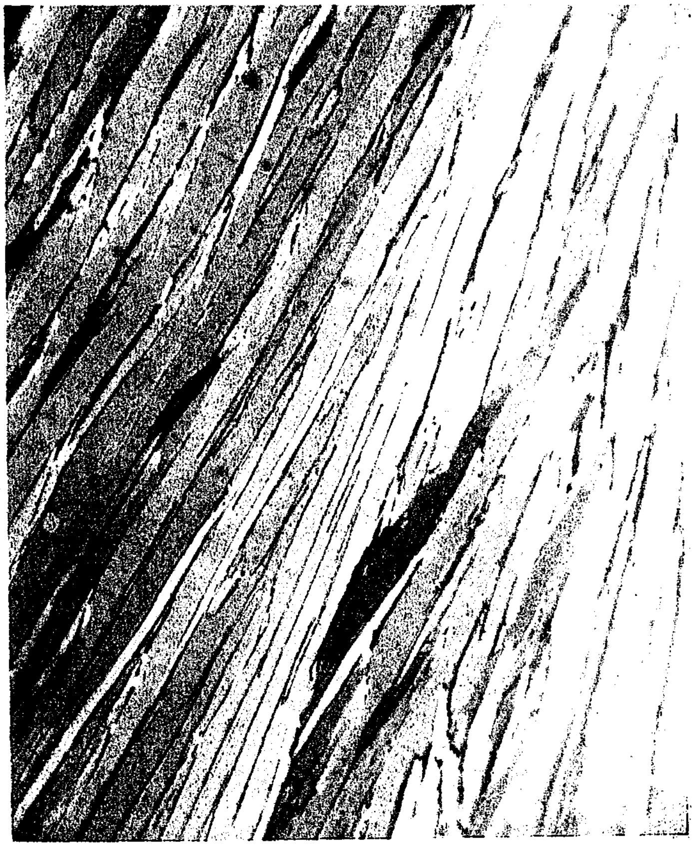


Figure 31. 2,4-DNT Simulant At Room Temperature (100X)

Figure 32. 2,4-DNT Simulant at Room Temperature (400X).

The 400X photograph clearly shows microvoids in the crystal structure similar to those present in solidified TNT.

Figure 33 shows a well-shaken mixture of Indramic 170C wax and supercooled 2,4-DNT with no emulsifier. The wax is dispersed as large droplets in the liquid 2,4-DNT. The droplets show some microcrystalline structure, but the wax is still fluid at this temperature. When the 2,4-DNT has crystallized, the wax fills the spaces between crystals of 2,4-DNT (Figure 34). This is similar to results with TNT reported in the literature (Reference 11). Incorporation of a poor emulsifier would probably give similar results.

At elevated temperatures (>100°C) with the Ganex WP-660 emulsifier Indramic 170C wax is dispersed largely as tiny droplets in the simulant (Figure 35).

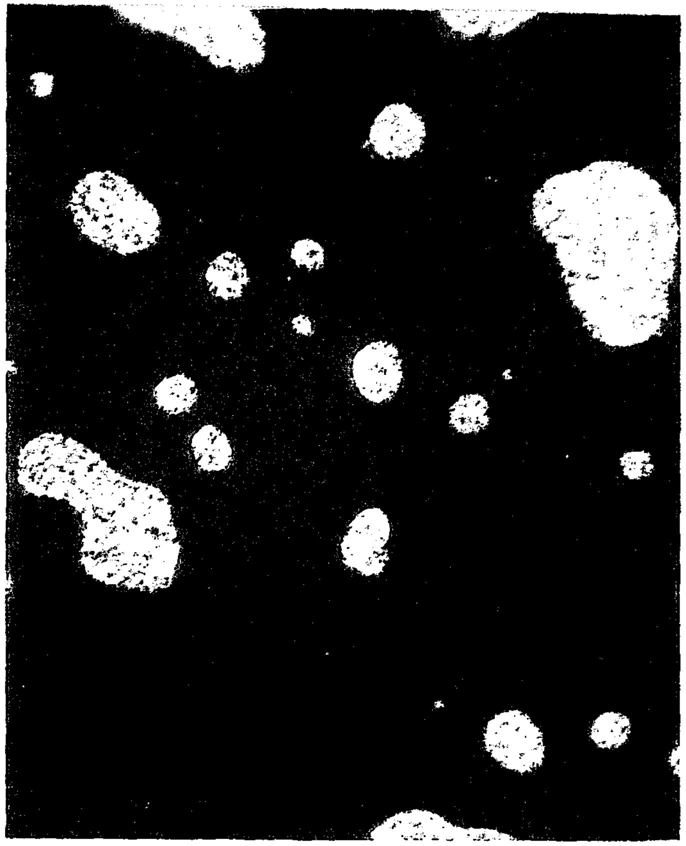


Figure 33. Indramic 170C Wax In Supercooled 2,4-DNT Simulant (100X)

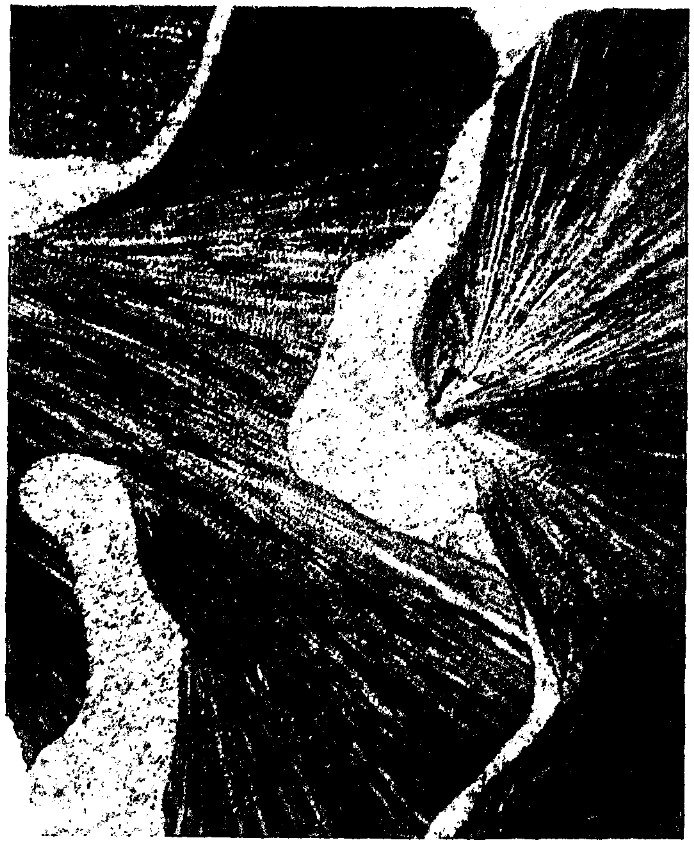


Figure 34. 2,4-DNT Crystals With Indramic 170C Wax (100X)

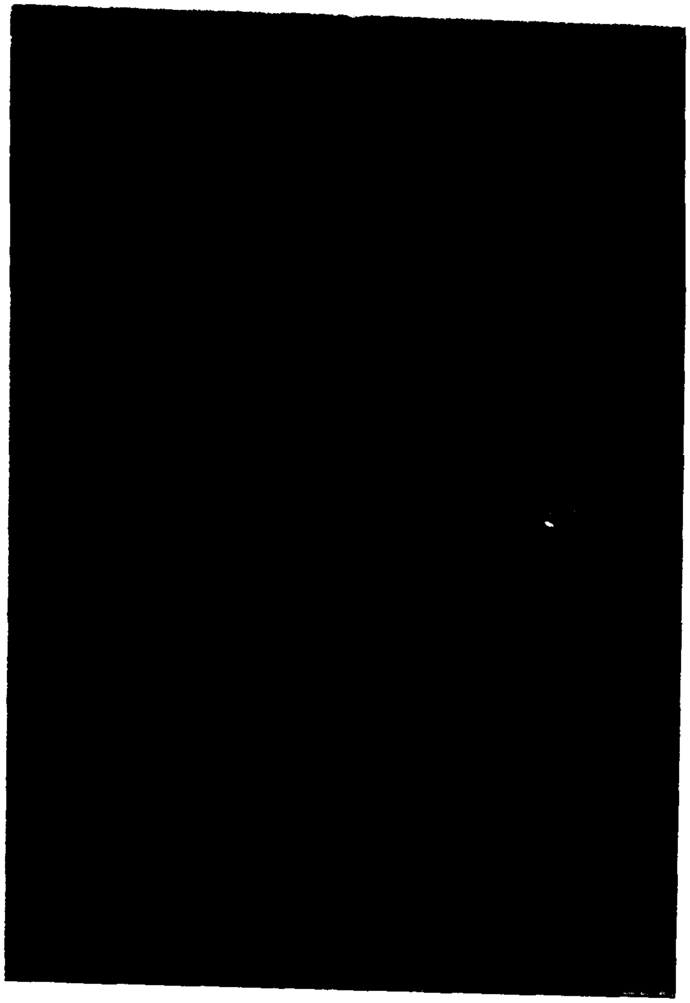


Figure 35. Indramic 170C Wax Droplets Dispersed with Ganex WP-660 in 2,4-DNT Simulant at Elevated Temperature (100X).

Figure 36 is a similar photomicrograph of Polywax 600 wax dispersed with the same emulsifier at elevated temperature. The droplets of wax in this less stable emulsion system are mostly larger than those formed with Indramic 170C wax.

Figure 37 shows these droplets starting to crystallize.

Figures 38 and 39 show the crystallized system of 2,4-DNT with Indramic 170C wax dispersed with Ganex WP-660 after cooling to room temperature. Unlike the situation without emulsifier where the wax mainly filled spaces between the crystals of simulant (Figure 34), the wax is dispersed in small droplets (orange) on the crystals of 2,4-DNT (green) and fills microvoids in the crystal mass.

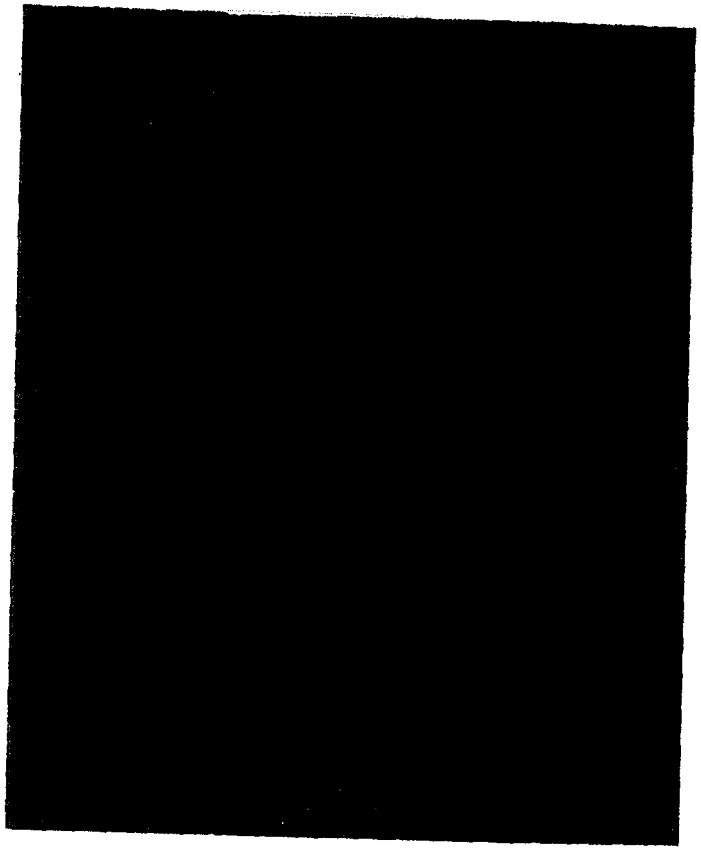


Figure 36. Droplets Of Polywax 600 Dispersed In 2,4-DNT Using Ganex WP-660 (100X)

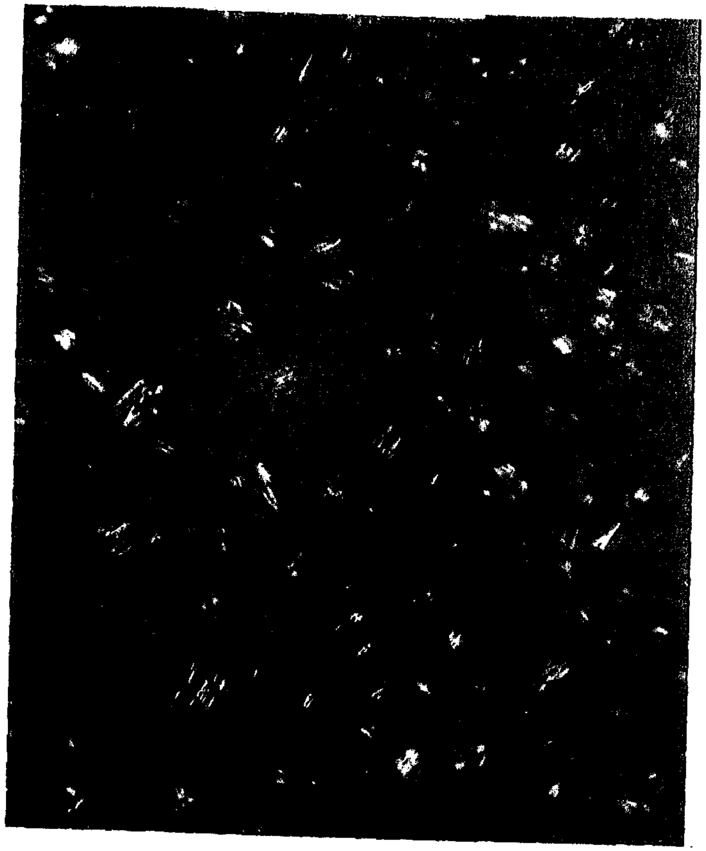


Figure 37. Droplets Of Partially Crystallized Polywax 600 Dispersed In 2,4-DNT Using Ganex WP-660 (100X)

Figure 38. Dispersed Indramic 170C Wax On
2,4-DNT Using Ganex WP-660
(100X In Color)

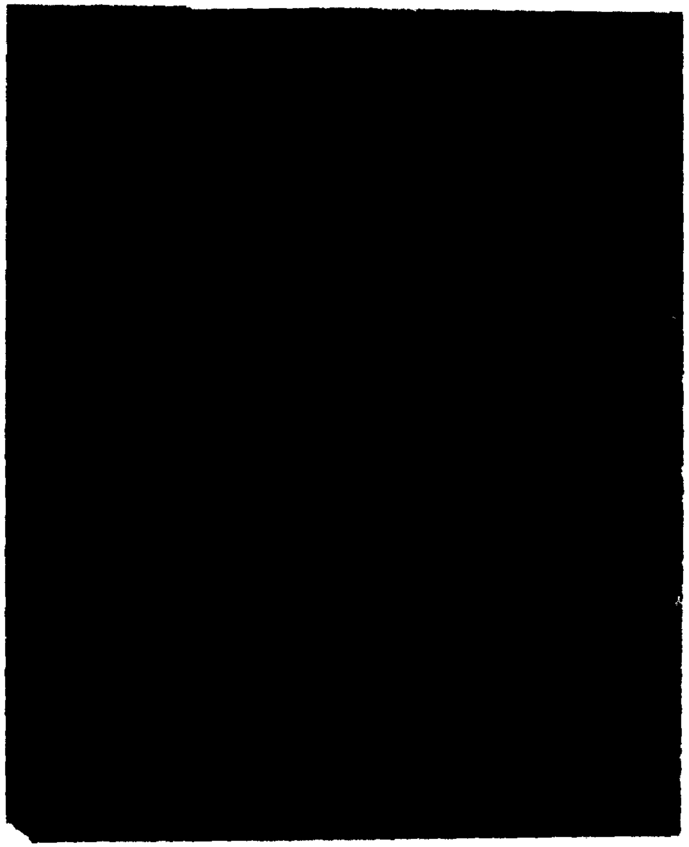


Figure 39. Dispersed Indramic 170C Wax On
2,4-DNT Using Ganex WP-660
(400X In Color)

The photomicrographs show that the effective Ganex resin emulsifiers produce stable emulsions by forming small spherical wax droplets that do not tend to aggregate quickly. On cooling to room temperature these wax droplets are dispersed among the simulant crystals where they fill microvoids and provide lubrication between crystals. The latter action can reduce frictional heat buildup in an explosive. The better wax dispersion should also quickly quench hotspots and suppress the self-accelerating reaction that leads to detonation.

Since the Ganex WP-660 emulsifier gave acceptable stability with Indramic 170C wax, binary and ternary blends of the Ganex emulsifiers were evaluated in an effort to improve performance. In aqueous systems blends of surface-active agents often provide better emulsification than single agents. Table 72 shows typical results of this study.

TABLE 72. BLENDS OF GANEX PRODUCTS AS EMULSIFIERS USING NITROETHANE SIMULANT

	Emulsifiers		Ratio	Emulsion Stability Break Time (min)
1	2	3		
V-216	V-220	---	100/0	5
"	"	---	75/25	3
"	"	---	50/50	3
"	"	---	25/75	0.5
"	"	---	0/100	5
"	WP-660	---	100/0	5
"	"	---	75/25	1
"	"	---	50/50	3
"	"	---	25/75	5
"	"	---	0/100	15
V-220	"	---	100/0	3
"	"	---	75/25	10
"	"	---	50/50	10
"	"	---	25/75	10
"	"	___	0/100	15
"	"	V-216	40/40/20	10
"	"	"	33/33/33	5
"	"	"	25/25/50	5
"	"	"	12.5/12.5/75	5
"	"	"	40/20/40	5
"	"	"	25/50/25	3
"	"	"	12.5/75/12.5	3

The blends did not provide greater emulsion stability than Ganex WP-660 alone. Similar results were obtained using 2,4-DNT simulant. Blends were also evaluated with Polywax 600. Again none of the blends outperformed Ganex WP-660 alone.

As shown in Table 68, Ganex WP-660 is an alkyl polylvinylpyrrolidone averaging one alkyl group containing thirty carbons per pyrrolidone ring. At MACH I's request ISP synthesized three products similar to WP-660 but containing more or less alkyl substitution. Table 73 shows the properties of these modified polymers. Their performance in the emulsion stability test using nitroethane simulant and Indramic 170C wax is shown in Table 74.

TABLE 73. PROPERTIES OF MODIFIED GANEX EMULSIFIERS

	Ganex 130	Ganex 330	Ganex 430
Appearance	-------- Off-white Solid ----------		
Bromine No.	22.8	14.4	11.7
Melting Pt.(°C)	55.1	56.5	57.1
Monomer Ratio Vinylpyrrolidone(VP)/Olefin	10/90	30/70	40/60

TABLE 74. PERFORMANCE OF THE MODIFIED GANEX EMULSIFIERS

Ganex	Alkyl Groups Per VP	Emulsion Stability Break Time (min)			
		Indramic 170C Wax		Polywax	
		Nitroethane	2,4-DNT	Nitroethane	2,4-DNT
130	2-3	0.5	0.5	0.5	0.5
WP-660	1	30	15	3	3
330	0.6	3	1	1	0.5
430	0.4	3	1	1	0.5

None of these experimental products provided stability approaching that given by the commercial product WP-660. Furthermore, combinations of the 130 and 330 variants, including a blend with average alkyl group:pyrrolidone ratio similar to that of WP-660, also failed to provide good emulsion stability (Table 75).

TABLE 75. MODIFIED GANEX EMULSIFIER BLENDS WITH INDRAMIC 170C WAX AND NITROETHANE

Emulsifier #1	Emulsifier #2	Ratio	Emulsion Stability Break Time (min)
Ganex 130	Ganex 330	10/90	1
"	"	20/80	1
"	"	25/75	1
"	"	40/60	1
"	"	50/50	0.5

TABLE 75 (continued)

"	"	60/40	0.5
"	"	90/10	0.5
Ganex 330	Ganex 430	50/50	3
Ganex 330	Ganex WP-660	50/50	3
Ganex 430	"	20/80	3
"	"	50/50	3
"	"	80/20	3

As Table 75 shows, combinations of the experimental materials with each other or with WP-660 were poor emulsifiers. Discussions with ISP revealed that some process solvent (*n*-butanol) remained in the synthesized products. ISP uses *n*-butanol as a process solvent for these lab prepared products but use *n*-hexanol in their commercial process. To determine if butanol could affect the emulsion stability test, it was added in the appropriate concentration to the commercial products WP-660, V-220 and V-216. As Table 76 shows, the butanol did not adversely affect emulsion stability.

TABLE 76. EFFECT OF BUTANOL ON EMULSION STABILITY OF INDRAMIC 170C WAX IN NITROETHANE

Ganex Emulsifier	% Butanol	Emulsion Stability Break Time (min)
WP-660	3.1	30
	0	30
V-220	3.1	10
	0	5
V-216	3.1	1
	0	1

Four more variants of the Ganex WP-660 structure were synthesized in an effort to increase emulsion stability. The commercial Ganex products are manufactured by placing the vinylpyrrolidone (PVP) and olefin monomers in a reaction vessel with the initiator. There the vinylpyrrolidone rapidly homopolymerizes, and then the olefin grafts onto the PVP chain. To prepare the new experimental variants of Ganex WP-660, preformed PVP of selected molecular weight was graft-alkylated with C_{30+} olefin. The properties of the resulting experimental Ganex emulsifiers are shown in the following table.

TABLE 77. EXPERIMENTAL VARIANTS OF GANEX WP-660

	9965-39B (K-30)	9965-39C (K-60)	9965-39D (K-90)	9965-40 (K-120)
Appearance	---------- Off-white flake -----------			
Solids,%	98.4	98.3	98.9	98.7
Relative Viscosity @30 °C(1)	1.31	1.26	1.31	1.29
Br Number	6.02	7.17	7.09	6.51
% Nitrogen	2.22	2.15	2.15	2.23
Melting Point (°C)	62	62	63	62
(MW of Polyvinylpyrrolidone (2)	40,000	220,000	700,000	>700,000

(1) 5% Solution in toluene
(2) Viscosity average molecular weight

The molecular weights of the polyvinylpyrrolidones (PVP) used to synthesize the experimental polymers are shown in the table. The molecular weights of the products are less certain due to coiling of the molecule and may be lower than those of the starting PVPs.

Performance of the WP-660 variants with Polywax 600 or Indramic 170C in nitroethane is shown in Table 78.

TABLE 78. EXPERIMENTAL GANEX WP-660: EMULSION STABILITY IN NITROETHANE SIMULANT

Emulsifier	Wax	Emulsion Stability Break Time (min)
9965-39B	Polywax 600	45
9965-39C	"	45
9965-39D	"	30
9965-40	"	45
9965-39B	Indramic 170C	45
9965-39C	"	45
9965-39D	"	45
9965-40	"	45

The emulsion stability of the two waxes in the nitroethane simulant was dramatically improved by the modifications in molecular weight. All of the variants excelled commercial Ganex WP-660. However, when these variants were evaluated with live TNT at WL/MNME, they did not perform well. Emulsion stability with 2,4-DNT simulant was also poor (Table 79) and thus agreed with behavior in TNT.

TABLE 79. GANEX WP-660 VARIANTS: EMULSION STABILITY IN 2,4-DNT SIMULANT

Emulsifier	Wax	Emulsion Stability Break Time (min)
9965-39B	Polywax 600	0.5
9965-39C	"	0.5
9965-39D	"	1
9965-40	"	1
9965-39B	Indramic 170C	0.5
9965-39C	"	0.5
9965-39D	"	1
9965-40	"	1

Performance of the experimental Ganex samples illustrates how small changes in the structure of the emulsifier profoundly affect emulsification of the wax/TNT or simulant system. With aqueous emulsifiers, one would expect to see some degree of emulsification stability when blends of two emulsifiers such as Ganex 130 and Ganex 330 are blended in a ratio to simulate Ganex WP-660. The non-aqueous wax/simulant and wax/TNT systems seem much more sensitive to changes in structure of the emulsifier than is the case with aqueous systems.

The pyrrolidone structure is capable of forming salt-like ion-pair complexes with acidic species. The extent of the interaction is indicated by the infrared shift of the pyrrolidone carbonyl group. This reaction with acids provides a method to modify an emulsifier structure to give possibly synergistic combinations for better emulsification.

Ganex V-216 was reacted with several Rhodafac phosphoric acid partial esters and with a polybutadiene/maleic anhydride. Upon mixing, exotherms of 2-5°C were observed. Rhodofac RM 510, RE 610 and RS 710 are polyethoxyphosphate esters of dinonylphenol, nonylphenol and tridecyl alcohol, respectively. Lubrophos LF200 is a polyethoxyphosphate of dodecyl phenol. PBMA-10 is polybutadiene copolymerized with 10 % by wt. of maleic anhydride. Evaluations of these reaction products are shown in Table 80.

TABLE 80. EMULSION STABILITY OF GANEX V-216 ION-PAIR COMPLEXES IN NITROETHANE SIMULANT

Acidic Reactant	Wax	Emulsion Stability Break Time (min)
Rhodafac RM 510	Indramic 170C	4
"	Polywax 600	1
Rhodofac RE 610	Indramic 170C	2.5
"	Polywax 600	1
Rhodofac RS 710	Indramic 170C	2
Lubrophos LF 200	Indramic 170C	0.5
"	Polywax 600	0.5
PBMA-10	Indramic 170C	<0.5
"	Polywax 600	0.5

Although the results show that none of the ion-pair complexes gave good stability, the Rhodafac RM 510 complex performed better than unmodified Ganex V-216.

In aqueous emulsification, blends of surface-active agents commonly give better stability than a single emulsifying agent. Ganex V-216, V-220 and Ganex WP-660 were blended with a variety of other surface-active compounds and evaluated for emulsion stability. Tables 81, 82, and 83 show the results.

TABLE 81. EMULSION STABILITY OF BLENDS OF SURFACE ACTIVE AGENTS AND GANEX V-216 USING POLYWAX 600

Emulsifier #2	Ratio (1)	Simulant	Emulsion Stability Break Time (min)
Aerosol TR 70	20/80	Nitroethane	1
"	40/60	"	3
"	60/40	"	3
"	80/20	"	3
"	50/50(3)	2,4-DNT	1
Centrolene A	60/40	Nitroethane	5
"	80/20	"	1
Centrol IPUB	50/50(3)	2,4-DNT	0.5
Hamposyl 95L	50/50(3)	"	0.5
Hamposyl O	50/50(3)	"	1
Monawet MT80H2W	50/50(3)	"	0.5
	50/50(3)	"	0.5(2)
Zn Stearate	50/50	"	<0.5

(1) Ganex V-216/emulsifier #2
(2) Emulsifier and wax melted before adding simulant.
(3) 25/75 and 75/25 ratios gave similar results with regular blending or melting with wax.

TABLE 82. EMULSION STABILITY OF BLENDS OF SURFACE ACTIVE AGENTS AND GANEX V-220 USING POLYWAX 600 IN 2,4-DNT SIMULANT

Emulsifier #2	Ratio (1)	Emulsion Stability Break Time (min)
Aerosol TR 70	50/50(3)	1
Centrol IPUB	50/50(3)	0.5
Hamposyl 95L	50/50(3)	0.5
Hamposyl O	50/50(3)	1
Monawet MT80H2W	50/50(3)	0.5
Monawet MT80H2W	50/50(3)	0.5(2)

(1) Ganex V-220/emulsifier #2
(2) Emulsifier and wax melted before adding simulant
(3) 25/75 and 75/25 ratios gave similar results with regular blending or melting with wax.

TABLE 83. EMULSION STABILITY OF BLENDS OF SURFACE ACTIVE AGENTS AND GANEX WP-660 USING POLYWAX 600

Emulsifier #2	Ratio (1)	Simulant	Emulsion Stability Break Time (min)
Aerosol OT 100	50/50	Nitroethane	2
Aerosol TR 70	20/80	"	2
"	40/60	"	5
"	50/50	"	5
"	60/40	"	5
"	80/20	"	5
"	50/50(3)	2,4-DNT	1
Centrophase HR2B	50/50	Nitroethane	1
Centrol IPUB	50/50	"	5
"	50/50(3)	2,4-DNT	1
Centrolene A	20/80	Nitroethane	1
"	40/60	"	3
"	50/50	"	5
"	60/40	"	3
"	75/25	"	3
"	80/20	"	5
Hamposyl 95L	50/50(3)	2,4-DNT	0.5
Hamposyl O	50/50(3)	"	1
Monawet MT80H2W	50/50(3)	"	0.5
Igepon T77	50/50	Nitroethane	1
Kenamide E	50/50	"	<0.5
Kenamide S	50/50	"	<0.5
Kenamide S180	50/50	"	0.5
Kenamide S221	50/50	"	0.5
Monawet MT80H2W	50/50	2,4-DNT	1
"	50/50	"	0(2)
PBMA-10	50/50	Nitroethane	2
Santicizer 148	90/10	"	0.5
"	50/50	"	0.5
SMA 1440	50/50	"	0.5
SMA 2625	50/50	"	<0.5
Zn Stearate	50/50	"	<0.5

(1) Ganex WP-660/emulsifier #2
(2) Emulsifier and wax melted before adding simulant.
(3) 25/75 and 75/25 ratio gave similar results with standard blending or melting with wax.

Aerosol OT and TR 77 are di(2-ethylhexyl) and ditridecyl sulfosuccinates, respectively. Centrophase, Centrolene A and Centrol IPUB are lecithins. The blends of members of these two groups with Ganex WP-660 gave the most stable emulsions (2-5 minutes), marginally better than obtained with the Ganex emulsifier alone. The Hamposyl sarcosinates, Kenamide fatty amides, Monawet tridecyl sulfosuccinate in hexylene glycol, PBMA-10, Santicizer 148, SMA styrene/maleic copolymer esters and the zinc stearate did not improve the performance of Ganex WP-660.

Ganex WP-660 was also blended with a styrene/butadiene block copolymer (Kraton D1101) and evaluated for emulsion stability. The styrene block of the copolymer might be soluble in the polar nitro compound while the butadiene block might be soluble in the wax. Conversely, the polar nitro compound or the wax or the Ganex WP-660 might dissolve in a block of the copolymer causing it to swell. The viscosity of the polymer might also help stabilize the emulsion. Table 84 shows the performance of the blends.

TABLE 84. EMULSION STABILITY OF BLENDS OF GANEX EMULSIFIERS WITH STYRENE/BUTADIENE COPOLYMER USING NITROETHANE

Ganex	Ratio (2)	WAX	Emulsion Stability Break Time (min)
V-216	90/10	Indramic 170C	0.5
"	75/25	"	0.5
"	50/50	"	0.5
"	90/10	Polywax 600	0.5
"	75/25	"	0.5
"	50/50	"	0.5
WP-660	95/5	Indramic 170C	5
"	90/10	"	15
"	75/25	"	10
"	50/50	"	15
"	100/0	Polywax 600	3
"	95/5	"	5
"	90/10	"	10
"	85/15	"	10
"	80/20	"	5
"	75/25	"	2
"	50/50	"	3(1)
"	90/10	"	3(1)
"	85/15	"	10(1)
"	80/20	"	1(1)
V-216	90/10	"	3(1)
"	85/15	"	3(1)
"	80/20	"	1(1)

(1) Ganex emulsifier and Kraton D1101 heated to 100°C for 90 minutes before adding simulant.
(2) Ratio of Ganex surfactant to Kraton D1101.
(3) In nitroethane.

With normal blending, the Ganex WP-660 blends with Kraton D1101 increased the stability of the emulsion of Polywax 600 in nitroethane simulant to 10 minutes compared to 3 minutes with Ganex WP-660 alone. The blends did not give increased stability when Ganex V-216 was used or with Indramic 170C wax.

To determine if longer contact time of Kraton D1101 with the emulsifier might increase the solubility of one in the other and improve stability, Ganex surfactant and Kraton D1101 (10, 15 and 20%) were heated to 100°C for 90 minutes before adding simulant. Both Ganex WP-660 and Ganex V-216 were evaluated. Kraton D1101 at 20% concentration swelled to fill the volume of Ganex WP-660. At 15% and 10% concentration there was less swollen Kraton D1101 than would be expected. Ganex V-216 with 20% Kraton D1101 exhibited less swelling than Ganex WP-660 with 10% Kraton. At 15% Kraton D1101 the emulsion stability of Polywax 600 with Ganex WP-660 was 10 minutes, the same as was obtained by the usual blending procedure. At 10 and 20% Kraton D1101 concentration stability was reduced. Emulsion stability of Indramic 170C wax with Ganex V-216 and Kraton D1101 was not acceptable, but it was better than achieved by the usual blending procedure.

When the emulsion breaks in the blends containing Kraton D1101, the top layer is hazy. Without Kraton D1101 it is clear. This haze is due to Kraton D1101 not being significantly soluble in the mix, but swelling because it dissolves Ganex surfactant, nitroethane and/or wax.

Ganex WP-660 blended with 10-15% Kraton D1101 by the usual method proved to be a good emulsifier for Polywax 600 in nitroethane. Thus a major objective of Task 4 was achieved. The effectiveness of the blend has been confirmed by live miscibility tests at WL/MNME. It should be noted that the blend ratio has not been optimized; a wider range of ratios should be tested.

Kraton G1650 was ineffective with Ganex WP-660 or Ganex V-216 for emulsifying either Polywax 600 or Indramic 170C with nitroethane. Emulsion stability was half a minute or one minute for 10, 20 and 30% levels of Kraton. Kraton G1650 differs from Kraton D1101 by having ethylene/butylene rather than butadiene as the soft polymer block.

Kraton D1101 at 10, 20 or 30% in Aerosol TR70, Centrol IPUB lecithin, or PBMA 10 was ineffective for emulsifying Indramic 170C with nitroethane. Emulsion stability in all cases was only half a minute.

Kraton D1101 at 10, 20 or 30% with Ganex WP-660 was ineffective in emulsifying Polywax 500. Emulsion stability was only 1 minute in each case.

b. Amine Salt Emulsifiers

Amine salts of sulfonic, carboxylic and phosphoric acids were evaluated to determine if emulsion stability patterns could be related to chemical structure. Since the nitrogen in Ganex surfactants may be a major reason for their effectiveness, amine salts were studied. These salts also provide an easy route to varying polarity of the molecules. The hydrophilic and lipophilic groups on the surface-active molecule may be changed by discrete units, and the optimum carbon number of the lipophilic portion may be found. Blending of two or more salts might also "fine tune" the performance of the emulsifying system. Table 85 shows the results obtained when a dodecylbenzenesulfonic acid (Biosoft S-100) was reacted with various amines and evaluated in the emulsion stability test.

TABLE 85. EMULSION STABILITY USING AMINE SALTS OF DODECYLBENZENESULFONIC ACID (1)

Amine	Trade Name	Emulsion Stability Break Time (min)	
		Indramic 170C	Polywax 600
Amyl	---	<0.5	<0.5
Dodecyl	Armeen 12D	<0.5	<0.5
Octadecyl	Armeen 18D	<0.5	---
Oleyl	Armeen OL	<0.5	<0.5

(1) Nitroethane simulant

The amine used to prepare the salt of dodecylbenzenesulfonic acid was varied from a carbon number of 5 in the amyl salt to 18 with the octadecyl salt. The oleyl salt was evaluated because the solubility of unsaturated moieties differs from that of their saturated counterparts and can produce differences in surface activity. The results showed no trend and good emulsion stability was not achieved.

To narrow further the differences among the amine salts and avoid possibly missing an optimum carbon number or polarity, blends of the amine salts of the Biosoft S-100 dodecylbenzenesulfonic acid and Witconate P-1059, an isopropyl amine salt of dodecylbenzenesulfonic acid, were evaluated. The results obtained with these blends are given in Table 86.

TABLE 86. EMULSION STABILITY USING BLENDS OF AMINE SALTS OF BIOSOFT S-100 AND WITCONATE P-1059 (1)

Biosoft S-100 Amine Salt	Ratio (2)	Emulsion Stability Break Time (min)	
		Indramic 170C	Polywax 600
---	0/100	<0.5	<0.5
Amyl Amine	10/90	<0.5	---
"	30/70	<0.5	---
"	50/50	<0.5	---
Dodecyl Amine	10/90	<0.5	---
"	30/70	<0.5	---
"	50/50	<0.5	---

(1) Nitroethane simulant
(2) Biosoft S-100 amine salt/Witconate P-1059

Again neither good emulsion stability nor trend in performance was observed. Next, amine salts were tested with the alkyl group on the benzenesulfonic acid reduced in size to a single carbon atom (toluenesulfonic acid). Blends with the isopropyl amine salt of dodecylbenzenesulfonic acid, Witconate P-1059, were also evaluated. Test results are shown in the Table 87.

TABLE 87. EMULSION STABILITY USING AMINE SALTS OF TOLUENESULFONIC ACID AND BLENDS WITH WITCONATE P-1059 (1)

Toluenesulfonic Amine salt	Ratio (2)	Emulsion Stability Break Time (min)
Dodecyl Amine	100/0	<0.5
"	50/50	<0.5
"	30/70	<0.5
"	10/90	<0.5
Octadecyl Amine	100/0	<0.5

(1) Indramic 170C wax and nitroethane simulant
(2) Toluenesulfonic amine salt/Witconate P-1059

Again no trend appeared and stability was poor.

Triethanolamine (TEA) contains hydroxyl groups that affect solubility and surface activity of its salts. Dodecylbenzenesulfonic acid salts of this amine were prepared and blended with other amine salts for testing. Table 88 shows the results.

TABLE 88. EMULSION STABILITY USING BLENDS OF TEA SALT OF BIOSOFT S-100 AND VARIOUS ALKYLBENZENESULFONIC SALTS (1)

Amine	Sulfonic acid	Ratio (2)	Emulsion Stability Break Time (Min.)
Amyl	Toluene	80/20	<0.5
"	"	70/30	<0.5
"	"	50/50	<0.5
"	Dodecylbenzene	90/10	<0.5
"	"	80/20	<0.5
"	"	70/30	<0.5
"	"	50/50	<0.5
Dodecyl	Toluene	70/30	<0.5
"	"	50/50	<0.5
"	"	30/70	
"	Dodecylbenzene	10/90	<0.5
"	"	20/80	<0.5
"	"	30/70	<0.5
Oleyl	Toluene	10/90	<0.5
"	"	30/70	<0.5

(1) Indramic 170C wax and nitroethane simulant
(2) Amine Alkylbenzenesulfonate salt/TEA Dodecylbenzenesulfonate

Again emulsion stability was poor and no trend emerged. Amine salts of carboxylic acids were also synthesized and tested. Table 89 shows the test results.

TABLE 89. EMULSION STABILITY USING AMINE SALTS OF CARBOXYLIC ACIDS WITH NITROETHANE SIMULANT

Amine	Carboxylic Acid	Emulsion Stability Break Time (min)	
		Indramic 170C	Polywax 600
Amyl	Dimer acid	---	0.5
Dodecyl	Caprylic	<0.5	<0.5
"	Oleic	<0.5	<0.5
"	Dimer acid	---	0.5
Octadecyl	Caprylic	<0.5	---
"	Oleic	<0.5	---
Oleyl	Oleic	<0.5	<0.5
Morpholine	Oleic	---	0.5
"	Dimer acid		
Hydroxyethyl pyrrolidone	Oleic	---	0.5
"	Dimer acid	---	0.5
N-Tallow-1,3-diaminopropane	"	---	0.5

TABLE 89 (continued)

N-Tallow -1,3-diaminopropane diacetate	"	---	0.5
N,*N*,*N*-Tris (2-hydroxyethyl) -tallow-1,3-diamino propane	"	---	0.5
N,*N*,*N*-Polyoxyethylene *N*-tallow- -1,3-diaminopropane	"	___	0.5
Propomeen T/12	"	---	0.5
Triamine T	"	---	0.5

Dimer acid (Hystrene 3695) is a mixture of C_{36} dibasic acids formed by condensation of C_{18} unsaturated monobasic fatty acids. A variety of amine/carboxylic acid combinations did not provide good emulsion stability or indication of a trend. Again, blends of the amine salts of caprylic acid were evaluated to ensure that optimum polarity was not being missed. Test results are shown in Table 90.

TABLE 90. EMULSION STABILITY USING BLENDS OF AMINE SALTS OF CAPRYLIC ACID (1)

Caprylic salt 1 Amine	Caprylic salt 2 Amine	Ratio (2)	Emulsion Stability Break Time (min)
Dodecyl	Oleyl	50/50	<0.5
Octadecyl	Dodecyl	50/50	<0.5
"	Oleyl	50/50	<0.5

(1) Indramic 170C wax and nitroethane simulant
(2) Salt 1/salt 2

These blends also showed poor stability, so several carboxylic acids were neutralized with TEA, blended with alkylbenzenesulfonic acid amine salts and tested. Results are shown in Tables 91 and 92.

TABLE 91. EMULSION STABILITY USING BLENDS OF TEA SALTS OF CARBOXYLIC ACIDS WITH WITCONATE P-1059 (1)

Carboxylic Acid	Ratio (2)	Emulsion Stability Break Time (min)
Caprylic	10/90	<0.5
"	30/70	<0.5

TABLE 91 (continued)

Oleic	10/90	<0.5
"	30/70	<0.5
Dimer Acid	10/90	<0.5
"	30/70	<0.5
Dimer Acid (3)	10/90	<0.5
"	30/70	<0.5
Dimer Acid (4)	10/90	<0.5
"	30/70	<0.5

(1) Indramic 170C wax and nitroethane simulant
(2) TEA carboxylic salt/Witconate P-1059
(3) Neutralized 75% of acid with TEA
(4) Neutralized 50% of acid with TEA

TABLE 92. EMULSION STABILITY USING BLENDS OF TEA SALTS OF CARBOXYLIC ACIDS WITH TEA BIOSOFT S-100 SALT (1)

Carboxylic Acid	Ratio (2)	Emulsion Stability Break Time (min)
Oleic	10/90	<0.5
"	30/70	<0.5
Dimer Acid	10/90	<0.5
"	30/70	<0.5
Dimer Acid (3)	10/90	<0.5
"	30/70	<0.5
Dimer Acid (4)	10/90	<0.5
"	30/70	<0.5

(1) Indramic 170C wax and nitroethane simulant
(2) TEA carboxylic salt/TEA Biosoft S-100 salt
(3) Neutralized 75% of acid with TEA
(4) Neutralized 50% of acid with TEA

None of these combinations resulted in good stability or suggested a pattern that might lead to better emulsifiers based on these carboxylic acids. Polymeric materials often show higher efficiency in surface active applications than agents of lower molecular weight. Therefore, PBMA-10, a polybutadiene polymer modified with 10% by weight of maleic anhydride, was reacted with various monomeric and polymeric amines and then tested for emulsion stability. A wide range of carbon numbers and polarity was thus obtained. These results are shown in Table 93.

TABLE 93. EMULSION STABILITY USING AMINE SALTS OF PBMA-10 (1)

Amine	Emulsion Stability Break Time (min)	
	Indramic 170C	Polywax 600
Amyl	<.05	<.05
Dodecyl	<.05	<.05
Octadecyl	<.05	<.05
Dimethyloleyl	<.05	<.05
Dicocoalkyl-methyl	<.05	<.05
Oleyl	<.05	<.05
Hydroxyethyl-pyrrolidone	0.5	0.5
TEA	<.05	<.05
Hi Tech 646	(2)	(2)
Hi Tech 648	0.5	0.5
LOA 565	0.5	0.5
Paranox 106	(2)	(2)
Paranox 147	(2)	(2)

(1) Nitroethane simulant
(2) Too viscous to mix

The Hi Tech 646 and 648 are succinimide-containing polymers manufactured by Ethyl. Paranox 106 and 147 from Exxon are nitrogen-containing polymers used as lube oil dispersants. LOA 565 from DuPont is an amino polyester used as a lube oil additive. The salts gave no apparent emulsion stability; several were too viscous to mix into the system.

Phosphate esters are common surfactants used in a variety of applications including emulsification. Reaction of the partial esters of these compounds with amines provides another series of amine salts with differing polarities due to the phosphate group. The phosphate esters used to synthesize amine salts were Rhodofac RM510, RE610, and RS710 as well as Lubrophos LF200. They are polyethoxyphosphate esters of dinonylphenol, nonylphenol, tridecyl alcohol and dodecylphenol, respectively. The emulsion stabilities provided by amine salts of these phosphate esters are shown in Table 94.

TABLE 94. EMULSION STABILITY USING AMINE SALTS OF POLYETHOXYPHOSPHATE ESTERS (1)

Amine	Phosphate Ester	Emulsion Stability Break Time (min)	
		Indramic 170C	Polywax 600
Amyl	RM510	<0.5	<0.5
"	RE610	<0.5	---

TABLE 94 (continued)

"	RS710	<0.5	---
Dodecyl	RM510	<0.5	<0.5
"	RE610	<0.5	---
"	RS710	<0.5	---
Oleyl	RM510	<0.5	---
"	RE610	<0.5	---
"	RS710	<0.5	---
"	RS710	<0.5	---
Dimethyloleyl	RE610	<0.5	---
"	RS710	<0.5	---
Hydroxyethyl-Pyrrolidone	LF200	---	0.5
"	RM510	---	0.5
TEA	RM510	<0.5	<0.5
"	RE610	<0.5	---
"	RS710	<0.5	<0.5

(1) Nitroethane simulant

As the table shows, all of the salts performed poorly.

c. Other Nitrogen-Containing Emulsifiers

Since Ganex surfactants contain nitrogen in the hydrophilic end of the monomer and provide good emulsification with Indramic waxes, several related nitrogen-containing products used as emulsifiers or dispersants were tested. ISP has recently commercialized two *N*-alkyl-2-pyrrolidones (Surfadones) that are highly surface active, reduce surface tension, and provide good wetting. Their structure is similar to the Ganexes, but they are monomeric. Test results are shown in Table 97.

TABLE 95. EMULSION STABILITY USING *N*-ALKYL-2-PYRROLIDONES AND BLENDS (1)

Pyrrolidone Alkyl Group	Emulsifier #2	Ratio (2)	Emulsion Stability Break Time (min)	
			Indramic 170C	Polywax 600
Octyl	---	---	0.5	0.5
Dodecyl	---	---	0.5	0.5
Octyl	Aerosol TR70	80/20	0.5	0.5
Dodecyl	Aerosol TR70	80/20	0.5	0.5
Octyl	Igepon T77	80/20	0.5	0.5
Dodecyl	Igepon T77	80/20	0.5	0.5

(1) Nitroethane simulant
(2) Ratio of alkylpyrrolidone/emulsifier #2

Alone the Surfadones gave poor stability. Blends with Aerosol TR70 (sodium tridecylsulfosuccinate) and Igepon T77 (sodium oleoyl-methyltaurate) were no better.

Solsperse dispersants are proprietary nitrogen-containing products. They consist of polymers and monomeric pigment chemicals. Table 96 shows that, except for Solsperse 5000 with Polywax 600, they did not provide good emulsion stability.

TABLE 96. EMULSION STABILITY USING SOLSPERSE EMULSIFIERS AND BLENDS (1)

Solsperse Emulsifier #1	Solsperse Emulsifier #2	Ratio (2)	Emulsion Stability Break Time (min) Indramic 170C	Polywax 600
5000	---	---	0.5	15
13345	---	---	0.5	0.5
17000	---	---	0.5	---
13345	5000	90/10	0.5	0.5
24000	5000	90/10	0.5	0.5

(1) Nitroethane simulant
(2) Ratio of Emulsifer #1/#2

Several tests of Solsperse 5000 with Polywax 600 in nitroethane resulted in good emulsion stability, so a specimen was sent to WL/MNME for live testing. However, when the surfactant proved to be incompatible with TNT (Figure 8), testing was discontinued.

Lubrizol produces lube oil dispersants containing substituted succinimides. Several variations of this structure were provided by Lubrizol for evaluation in this program (Table 97).

TABLE 97. EMULSION STABILITY USING LUBRIZOL EMULSIFIERS (1)

Lubrizol Emulsifier	Emulsion Stability Break Time (min) Indramic 170C	Polywax 600
2633	---	0.5
OS 22277AJ	0.5	0.5
OS 47550W	0.5	0.5
OS 87440A	0.5	1

(1) Nitroethane simulant

These dispersants did not provide acceptable emulsion stability.

A number of other commercial surface-active agents and dispersants containing nitrogen were evaluated. In many instances the compositions of these materials are proprietary and only generic descriptions of their compositions are available. These products are identified in Table 98; their poor performance is shown in Table 99.

TABLE 98. COMPOSITION OF NITROGEN-CONTAINING EMULSIFIERS

Emulsifier Name	Composition
Alkaterge C	Octadecyloxazoline
Antiterra 204	Acidic ester salt of polyamine amides
Antiterra U	Acidic ester salt of polyamine amides
Armac HT	Tallow amine acetate
Duomeen T	*N*-Tallow-1,3-diaminopropane diacetate
Duomeen TDO	*N*-Tallow-1,3-diaminopropane dioleate
Ethoduomeen T/13	Tris(2-Hydroxyethyl)-*N*-tallow-1,3-diaminopropane
Ethoduomeen T/25	Polyoxyethylene-*N*-tallow-1,3-diaminopropane
Hi Tech 644	Succinimide containing polymers
Hi Tech 646	Succinimide containing polymers
Indulin W	Aminolignin sulfonate
Kenamine DP3680	Dimer diprimary amine
Kenamine DD3695	Dimer diprimary amine
LOA 565	Aminopolyester
Paranox 106	Amino containing polymer
Propomeen T12	Propoxylated *N*-tallow amine
Triamine T	*N*-Tallow-alkyldipropylene triamine

TABLE 99. EMULSION STABILITY USING NITROGEN-CONTAINING EMULSIFIERS (1)

Emulsifier	Emulsion Stability Break Time (min)	
	Indramic 170C	Polywax 600
Alkaterge C	---	0.5
Antiterra 204	---	<0.5
Antiterra U	---	<0.5
Armac HT	0.5	0.5
Duomeen T	0.5	0.5
Duomeen TDO	0.5	0.5
Ethoduomeen T/13	0.5	0.5
Ethoduomeen T/25	0.5	0.5
Hi Tech 644	0.5	1
Hi Tech 646	0.5	1
Indulin W	<0.5	---

TABLE 99 (continued)

Kenamine DD3680	0.5	0.5
Kenamine DD3695	0.5	0.5
LOA 565	0.5	1
Paranox 106	0.5	1
Propomeen T12	0.5	0.5
Triamine T	0.5	0.5

(1) Nitroethane simulant

d. Coupling Agents or Plasticizers As Emulsifiers

Another approach taken to develop an emulsifier for the wax/TNT simulant system was to test materials that might act as coupling agents for the wax and nitro compound. This is often done to blend two otherwise immiscible polymers. A different portion of the coupling agent structure is compatible with each polymer. The polybutadiene/maleic anhydride adduct that was tested in Phase I appeared to be a potential coupling agent. The maleic anhydride or ester portion of the structure might be compatible with the nitro compounds, which have similar solubility parameters [11-12 $(cal/cm^3)^{0.5}$], while the butadiene portion could be compatible with the waxes. However, PBMA-10 alone did not provide good emulsion stability. The polymer was also blended with co-emulsifiers and reacted with hydroxyl-terminated compounds in an attempt to achieve acceptable emulsion stability. Table 100 shows results of testing blends of the polymer PBMA-10, which contains 10% by weight of maleic anhydride, with several other dispersing agents and potential reactants.

TABLE 100. EMULSION STABILITY USING BLENDS OF PMBA-10 WITH CO-EMULSIFIERS (1)

Co-emulsifier	Ratio (2)	Emulsion Stability Break Time (min)	
		Indramic 170C	Polywax 600
Kenamide E	50/50	<0.5	---
Kenamide S	75/25	0.5	0.5
"	50/50	<0.5	---
"	25/75	0.5	0.5
Kenamide S180	50/50	<0.5	---
Kenamide S221	75/25	0.5	0.5
"	50/50	<0.5	<0.5
"	25/75	0.5	0.5
Kraton D1101	25/75	---	0.5
"	25/75	---	0.5
Poly bd R45HT	5/95	0.5	---
"	10/90	0.5	---
"	20/80	1	0.5

TABLE 100 (continued)

"	60/40	0.5	---
"	75/25	0.5	---
Unilin 425	25/75	1	1
"	75/25	1	1
Unilin 550	25/75	1	1
"	75/25	1	1
Unilin 700	25/75	1	1
"	75/25	1	1

(1) Nitroethane simulant
(2) Ratio of PBMA-10/Co-emulsifier

The PBMA-10 blends did not provide acceptable emulsion stability with Indramic 170C or Polywax 600. However the results obtained with the Unilin alcohols suggested that synthesis of esters of these long carbon chain compounds might hold promise. Esters were also prepared using Unithox compounds, which are hydroxy-terminated ethoxylated Unilin alcohols. Table 101 shows the results of testing these esters.

TABLE 101. EMULSION STABILITY USING PBMA-10 ESTERS AND BLENDS(1)

Emulsifier #1	Emulsifier #2	Ratio (2)	Emulsion Stability Break Time (min)	
			Indramic 170C	Polywax 600
PBMA-10-Unilin 425 ester	---	---	3	3
"	PBMA-10	75/25	0.5	1
"	"	50/50	1	1
"	"	25/75	1	0.5
"	Unilin 425	75/25	<.5	<.5
"	"	50/50	<.5	<.5
"	"	25/75	<.5	<.5
PBMA-10-Unilin 550 ester	---	---	3	3
PBMA-10-Unilin 700 ester	---	---	0.5	0.5
PBMA-10-Unithox 450 ester	---	---	<.5	<.5
PBMA-10-Unithox 480 ester	---	---	<.5	<.5
PBMA-10-Unilin 550 ester	---	---	<.5	<.5

(1) Nitroethane simulant
(2) Ratio of emulsifier #1/#2

As the table shows, the preformed esters from Unilin 425 and 550 provided improved, but still not acceptable, levels of emulsion stability with both Indramic 170C and Polywax 600. Blending the ester with PBMA-10 or Unilin 425 degraded stability. Esters prepared from the Unithox alcohols gave poor emulsion stability with both waxes.

Available styrene/maleic copolymers and esters have the potential of enhancing emulsification by a coupling mechanism. The anhydride or the ester might provide miscibility with nitro compounds while the styrene portion may be compatible with the wax. Styrene/maleic copolymers, which are used as pour point depressants in lubricating oils, function by adsorption on wax crystals (Reference 38). The copolymers are sold by Atochem. Their structures are shown in Table 102.

TABLE 102. STRUCTURES OF STYRENE/MALEIC COPOLYMERS

Trade Name	Styrene/Maleic Ratio	Resin Type	Molecular Weight
SMA 1000	1/1	Unmodified	1600
SMA 3000	3/1	Unmodified	1900
SMA 1440	1/1	Half Ester	2500
SMA 2625	2/1	Half Ester	1900
SMA 17352	1/1	Half Ester	1700

The emulsion stabilization by the commercial resins was evaluated in Phase I and found to be inadequate. Table 103 shows results obtained when the resins were blended with co-emulsifiers.

TABLE 103. EMULSION STABILITY USING STYRENE/MALEIC COPOLYMERS, ESTERS AND BLENDS (1)

Copolymer	Emulsifier #2	Ratio (2)	Emulsion Stability Break Time (min)	
			Indramic 170C	Polywax 600
SMA 1000	---	---	0.5	---
SMA 3000	---	---	---	0.5
SMA 1000	SMA 1440	50/50	<0.5	---
"	SMA 2625	50/50	<0.5	---
"	SMA 17352	50/50	<0.5	---
"	Igepon T77	50/50	---	<0.5
"	Solsperse 13345	50/50	---	<0.5
SMA 1440	SMA 2625	50/50	<0.5	---
"	SMA 17352	50/50	<0.5	---
"	Igepon T77	50/50	<0.5	<0.5
"	Solsperse 13345	50/50	1	<0.5
"	Rhodafac RM510	50/50	<0.5	---

TABLE 103 (continued)

SMA 2625	Igepon T77	75/25	0.5	0.5
"	"	50/50	1	0.5
"	"	50/50	0.5 (3)	---
"	"	25/75	0.5	0.5
"	Solsperse 13345	75/25	1.5	---
"	"	50/50	1	<0.5
"	"	25/75	<0.5	---
"	Elvax 310	50/50	<0.5	---
"	Elvax 500W	50/50	<0.5	---
"	Elvax 40W	50/50	<0.5	---
"	PBMA-10	50/50	<0.5	---
SMA 17352	Igepon T77	50/50	<0.5	---
"	Solsperse 13345	50/50	<0.5	---

(1) Nitroethane simulant unless noted.
(2) SMA resin/emulsifier #2
(3) 2,4-DNT simulant

Blending the commercial resins with co-emulsifiers did not produce satisfactory emulsion stability. Coupling ability of these resins was also changed by reaction with longer chain alcohols. The commercial resins are partially esterified with isopropyl and other alcohols of low molecular weight. Longer chain alcohols would be expected to improve compatibility with wax. Therefore SMA 1000 and 3000 were reacted with a branched dodecyl alcohol (Exxal 12) and a 24 carbon chain linear alcohol (Unilin 350) to form partial esters. Emulsion stability given by these esters and blends with co-emulsifiers is shown in Table 104.

TABLE 104. EMULSION STABILITY USING SYNTHESIZED SMA ESTERS AND BLENDS (1)

Copolymer Ester	Emulsifier #2	Ratio (2)	Emulsion Stability Break Time (min)	
			Indramic 170C	Polywax 600
SMA 1000-Exxal 12	---	---	0.5	0.5
"	---	---	0.5 (3)	---
"	Aerosol OT	80/20	0.5	0.5
"	"	60/40	0.5	0.5
"	"	50/50	0.5	0.5
"	"	40/60	0.5	0.5
"	"	20/80	0.5	0.5
"	Unithox 420	80/20	0.5	0.5
"	"	60/40	0.5	0.5
"	"	50/50	0.5	0.5
"	"	40/60	0.5	0.5
"	"	20/80	0.5	0.5

TABLE 104 (continued)

SMA 3000- Exxal 12	---	---	0.5	0.5
SMA 3000- Unilin 350	---	---	0.5	0.5
"	Unithox 350	80/20	0.5	0.5
"	"	60/40	0.5	0.5
"	"	50/50	0.5	0.5
"	"	40/60	0.5	0.5
"	"	20/80	0.5	0.5

(1) Nitroethane simulant unless noted.
(2) SMA resin/emulsifier #2
(3) 2,4-DNT simulant

The co-emulsifiers were Aerosol OT [di(2-ethylhexyl) sulfosuccinate] and two Unithox products (polyethoxylated long chain alcohols). Neither the synthesized esters nor their blends gave acceptable emulsification.

Many plasticizers are compatible with polymers such as polyvinyl chloride that have solubility parameters close to those of nitro compounds. A commercial tridecyl phthalate (Jayflex DTBD) and three phthalates prepared by reaction of the anhydride with long chain Unilin alcohols were tested as candidate emulsifiers. As shown in Table 105, the results were not encouraging.

TABLE 105. EMULSION STABILITY USING PHTHALATE ESTERS (1)

Alcohol	Alcohol Carbon No.	Emulsion Stability Break Time (min)	
		Indramic 170C	Polywax 600
Tridecyl	13	0.5	0.5
Unilin 425	32	0.5	0.5
"	"	0.5 (2)	---
Unilin 550	38	0.5	0.5
Unilin 700	49	0.5	0.5

(1) Nitroethane simulant unless noted.
(2) 2,4-DNT simulant

Nitrobenzoic esters were also evaluated. The nitrobenzoic group is expected to be compatible with the nitro compounds while a long chain ester group may be compatible with the wax. Such esters were synthesized by transesterification of ethyl *p*-nitrobenzoate. As Table 106 shows, they also did not perform well.

TABLE 106. EMULSION STABILITY USING NITROBENZOIC ESTERS (1)

Alcohol	Alcohol Carbon No.	Emulsion Stability Break Time (min) Indramic 170C	Polywax 600
Unilin 425	32	0.5	0.5
"	"	0.5 (2)	---
Unilin 550	38	0.5	0.5
"	"	0.5 (2)	---

(1) Nitroethane simulant unless noted.
(2) 2,4-DNT simulant

As the foregoing results indicate, neither coupling agents, commonly effective for compatibilizing polymers, nor specially tailored plasticizers provided adequate emulsion stability.

e. HLB Approach to Emulsification

The HLB method of identifying effective emulsifiers was described in Section V of this report. This approach was taken to select several blends of emulsifiers. Two surface active agents were combined with the blend ratio varied to provide incremental changes in the HLB value of the combination. If the wax/simulant system is amenable to this approach, an increase in stability time should be found at a certain HLB value. Results of tests based on this approach are shown in Tables 107 and 108.

TABLE 107. EMULSION STABILITY OF NITROETHANE SIMULANT AND POLYWAX 600 USING THE HLB APPROACH

Emulsifier #1 (HLB)	Emulsifier #2 (HLB)	Ratio (1)	HLB	Emulsion Stability Break Time (min)
Span 85	Brij 96	100/0	1.8	0.5
(1.8)	(12.4)	90/10	2.9	0.5
		80/20	3.9	0.5
		70/30	5.0	0.5
		60/40	6.0	0.5
		50/50	7.1	0.5
		40/60	8.2	0.5
		30/70	9.2	0.5
		20/80	10.3	0.5
		10/90	11.3	0.5
		0/100	12.4	0.5
Triton X-15	Triton X-45	100/0	3.6	0.5
(3.6)	(10.4)	90/10	4.3	0.5
		80/20	5.0	0.5

TABLE 107 (continued)

		70/30	5.6	0.5
		60/40	6.3	0.5
		50/50	7.0	0.5
		40/60	7.7	0.5
		30/70	8.4	0.5
		20/80	9.0	0.5
		10/90	9.7	0.5
		0/100	10.4	0.5
Centrol IPUB (4)	Centrolene A (10)	90/10	4.6	0.5
		70/30	5.8	0.5
		50/50	5.8	0.5
		40/60	7.6	0.5
		30/70	8.2	0.5
		10/90	9.4	0.5
Pluronic L-61 (3)	Pluronic F-68 (29)	95/5	4.3	0.5
		90/10	5.6	0.5
		85/15	6.9	0.5
		80/20	8.2	0.5
		75/25	9.5	0.5
		65/35	12.1	0.5
		60/40	13.4	0.5
		40/60	18.6	0.5
		30/70	21.2	0.5
		25/75	22.5	0.5
		15/85	25.1	0.5
		10/90	26.4	0.5
		5/95	27.7	0.5

(1) Emulsifier #1/Emulsifier #2

The first series of blends consisted of Span 85 and Brij 96. Span 85 is a sorbitan trioleate and Brij 96 is a polyoxyethylene oleyl ether manufactured by ICI. These two emulsifiers are widely used in aqueous systems. No indication of a favorable HLB is apparent.

The second series included octylphenol ethoxylates manufactured by Union Carbide under the Triton trade name. These are also widely used as surfactants and emulsifiers. Triton X15 with HLB of 3.6 and Triton X45 with HLB of 10.4 were blended and tested for stabilizing the nitroethane-Polywax 600 emulsion. The results were similar to the the first series.

The third series was based on blends of lecithin products from Central Soya. Centrol IPUB with HLB of 4.0 and Centrolene A with HLB of 10 are widely used as emulsifiers in the food industry. The blended lecithins proved to be poor emulsifiers of nitroethane/wax and showed no evidence of a favored HLB.

The fourth series covered the widest HLB range, using block copolymers of ethylene and propylene oxides (Pluronics) from BASF. These emulsifiers are widely used for dispersing pigments and insecticides. Again, no preferred HLB was evident.

Two emulsifier series were evaluated using 2,4-DNT simulant and both Indramic 170C and Polywax 600.

TABLE 108. EMULSION STABILITY OF 2,4-DNT SIMULANT AND WAXES BY THE HLB APPROACH

Emulsifier #1 (HLB)	Emulsifier #2 (HLB)	Ratio (2)	HLB	Emulsion Stability Break Time (min) Indramic 170C	Emulsion Stability Break Time (min) Polywax 600
HTBD-20 (4)	HTBD-50 (10)	100/0	4.0	0.5	0.5
		77/23	5.4	1	0.5
		62/38	6.3	1	0.5
		58/42	6.5	0.5	0.5
		51/49	7.0	1	0.5
		38/62	7.7	1	0.5
		25/75	8.5	0.5	0.5
		19/81	8.8	0.5	0.5
		9/91	9.4	1	0.5
		0/100	10.0	0.5	0.5
HTBD-20 (4)	Triton X-45 (10.4)	100/0	4.0	0.5	0.5
		77/23	5.5	0.5	0.5
		62/38	6.5	0.5	0.5
		58/42	6.7	0.5	0.5
		51/49	7.2	0.5	0.5
		38/62	7.9	0.5	0.5
		23/77	8.9	0.5	0.5
		0/100	10.4	0.5	0.5

HTBD-20 and 50 are ethoxylated hydroxyl terminated polybutadiene polymers made for MACH I by Ethoxy Corporation. Together or in combination with a Triton dispersant these emulsifiers failed to indicate a preferred HLB value with 2,4-DNT simulant.

The foregoing results using various emulsifier candidates did not identify favored HLB values for the NE/Polywax 600 or the wax/2,4-DNT systems. As noted in Section V, the HLB approach has limitations. In test procedures of the present program the emulsifier blends were not sufficiently good to show even slightly favorable trends. The standard miscibility test provides very little mechanical energy to emulsify the simulant-wax mixture. Consequently, a very efficient emulsifier such as a Ganex surfactant is required.

f. Other Emulsifiers

Several other types of emulsifier were evaluated for emulsion stabilization of the wax/nitro simulants. Union Carbide recently introduced a line of polyalkoxylated dimethyl siloxanes as emulsifiers and dispersants. As shown in Table 109, these proved to be quite ineffective.

TABLE 109. EMULSION STABILITY USING POLYALKOXYLATED DIMETHYL SILOXANES (1)

Silwet Emulsifier	Emulsion Stability Break Time (min)	
	Indramic 170C	Polywax 600
L7001	<0.5	<0.5
L7201	<0.5	<0.5
L7500	<0.5	<0.5
L7602	<0.5	<0.5
L7604	<0.5	<0.5
L7622	<0.5	<0.5
L77	<0.5	<0.5
L772	<0.5	<0.5

(1) Nitroethane simulant

Kenrich Petrochemicals offers several organotitanate surfactants. As shown in Table 110, these proved to be ineffective as emulsifiers.

TABLE 110. EMULSION STABILITY OF POLYWAX 600 USING ORGANOTITANATES (1)

Kenrich Emulsifier	Emulsion Stability Break Time (min)
KR46B	0.5
KR55	<0.5
LICA 12	<0.5
LICA 38	<0.5
LICA 44	0.5
NZ9	0.5
NZ12	0.5

(1) Nitroethane simulant

Oil-soluble petroleum sulfonates is a term used loosely to describe mixed mono- and dialkylbenzene sulfonates with an average of 18 to 23 alkyl carbon atoms or a sulfonate byproduct from the manufacture of white oil. The sodium salt of the latter has an equivalent weight of about 450-540. The sulfonates are also available as the calcium, magnesium and barium salts. These salts of divalent cations are available in neutral or overbased (about 100-400 base number) form. Some of these are excellent dispersants for motor oils or good emulsifiers in other applications.

Ten of these sulfonates were evaluated as emulsifiers for Indramic 170C and Polywax 600 in nitroethane or 2,4-DNT simulant. Emulsion stability was only 0.5 minutes in all cases. Properties of the sulfonates are shown in Table 111.

TABLE 111. PETROLEUM SULFONATES

	Alkyl Carbon No.	Equiv Weight As Na	Base No.	% Sulfonate
Aristonate L, Sodium(1)	18			60 min
Aristonate M, Sodium(1)	20			60 min
Aristonate H, Sodium(1)	23			60 min
Petronate 540 Sodium		540		61.5 min
Petronate HL Sodium		445		61.5 min
Neutral Barium Petronate		455		51 min
Basic Barium Petronate		495	69	42 min
Hybase M-400TG, Magnesium			392	29 min
Calcium Petronate 25CG		1080(2)	33	44 min
Hybase C-400G	22		409	

(1) Pilot Chemical Co., all others made by Witco Chemical Co.
(2) Molecular weight

4. EXPLOSIVE TESTING AT WL/MNME

To qualify for possible use in formulating a cast explosive composition, a candidate ingredient must not degrade thermal stability. WL/MNME screens candidates for chemical compatibility by DSC of a mixture of the candidate with the explosive components. A large depression of the characteristic exotherm indicates that the tested ingredient accelerates decomposition and therefore must be rejected. Table 112 shows the results of such tests on established ingredients as well as candidates showing promise in Phases I and II of the present program.

TABLE 112. COMPATIBILITY OF INGREDIENTS BY DSC

Explosive	Composition	Exotherm Onset (°C)	Peak(°C)
TNT	---	300	303
NTO	---	274	275.6
TNTO IV	Comp. D2 Wax	257.7	262.3
TNTO IV	Indramic 800/Ganex WP-660	262.9	266.2

TABLE 112 (continued)

TNTO IV	Petrowax 9508/Ganex WP-660	260.8	264.6
TNTO IV	Paxwax 7517/Ganex WP-660	260.2	264.4
TNTO IV	Polywax 600/2% NC/ 2% Lecithin	261.8	265.6
TNT	Polywax 600/Solsperse 5000	152.2	161.5
TNT	Indramic 170C/Aerosol TR70	254.1	275.8
TNT	Indramic 170C/Igepon T77	233.8	260.9

The compositions containing Ganex WP-660 showed exotherm shifts similar to that produced by Composition D2 wax and therefore are acceptable. Aerosol TR70 and Igepon T77 caused greater depression but were deemed safe enough to be tested for miscibility. Solsperse 5000 caused an exotherm shift large enough to preclude further testing.

Results of emulsion stability tests of candidate emulsifiers with TNT and waxes are shown in Table 113.

TABLE 113. STABILITY OF TNT EMULSIONS

Emulsifier	WAX	Separation (mL) at			
		5	10	15	20 min
Ganex V-216	Polywax 600	0.1	0.15	0.15	0.2
Ganex V-220	"	0.8	0.8	0.8	0.8
Ganex WP-660	"	1.2	1.2	1.2	1.2
Centrol 1PUB	"	0	0.2	0.4	0.5
Ganex Blend	"	0.4	0.4	0.4	0.4
Igepon T77	Indramic 170C	0.8T	0.8T	0.8T	0.8T
		1.5M	0.9M	0.8M	0.7M
Aerosol TR70	"	0.3	0.5	0.8	0.9
Ganex WP-660	"	0	0	0	0
Ganex V-216	"	0	0	0	0
Ganex WP-660	Indramic 800	0	0	0	0
Ganex V-216	"	0	0	0	0

(T) Top layer
(M) Middle layer

Ganex resin emulsifiers perform very well with the Indramic waxes but not with Polywax 600. The Ganex blend tested, a mixture of equal parts of the three commercial Ganex resin emulsifiers, permitted some phase separation with Polywax 600. Igepon T77 appeared to react slowly with TNT and did not form a stable emulsion. Aerosol TR70 did not give a good or stable emulsion with Indramic wax.

Table 114 shows that even at reduced concentrations Ganex WP-660 provided good, stable emulsions with TNT and other microcrystalline waxes.

TABLE 114. TNT EMULSION STABILITY USING GANEX WP-660 AT VARIOUS CONCENTRATIONS

Wax	Separation (mL) in 20 min Concentration (1) 10%	 5%	 1%	 .05%
Indramic 800	0	0	0(2)	0(2)
Petrowax 9508	0	0	0(2)	0(2)
Paxwax 7517	0	0	0	0(2)

(1) Wt % based on wax.
(2) Migration of TNT/wax but no layer.

WL/MNME technical personnel scaled up an explosive formulation using Ganex WP-660 as the emulsifier. The formulation consisted of 30% TNT, 40% NTO, 20% Al, 8.5% Indramic 800 wax and 1.5% Ganex WP-660 by weight. The TNT was loaded into the reactor and melted. At a temperature of about 90°C the molten TNT was a low viscosity, yellow-brown, clear liquid. Addition of the Ganex WP-660 caused the liquid to become opaque. Wax in small chunks was added and stirred until melted. The aluminum powder was added and the liquid mixture became gray and lumpy, but it remained very fluid. After about 5 minutes of mixing, the NTO was added scoop-wise. The mixture increased substantially in viscosity and resembled a very wet concrete mix. Stirring was continued for several minutes and then the mixture was allowed to stand. Very few small bubbles could be discerned in the mixture. There was no evidence of separation. Stirring was then resumed for approximately 20-30 minutes and the mixture was cast into four molds. Two of the molds were placed in an oven to cool slowly, and two were placed on a table to cool at room temperature. The remainder of the mix was poured onto a flat tray where it solidified rapidly. None of the surfaces of the in-process liquids or finished solids showed any evidence of gassing or bubbles. The castings appeared to be uniform solids without evidence of separation. The mold density, which provides a measure of voids and bubbles, was very high.

A further successful scale-up to six 500 pound bombs was made shortly after the preliminary scale-up discussed above indicated there should be no problems.

Explosive evaluations confirmed results with nitroethane simulant that 15-20% Kraton D1101 rubber with Ganex WP-660 gave Polywax 600 good emulsion stability (15 minutes) as shown in Table 115. Two other evaluations at the same emulsifier concentration of 20% of the wax had 15 and 20 minute stability.

Since Polywax 600 requires higher processing temperatures because of its higher melting point, WL/MNME was requested to evaluate similar Ganex WP-660/Kraton D1101 blends to emulsify lower melting point Polywax 500. The stability obtained was 20-30 minutes as shown in Table 115. Kraton forms a gel network in waxes, oils, and polymers imparting desirable flexibility, and impact strength. It should reduce or eliminate exudation of Polywax 500. Kraton concentrations that gave good emulsion stability were in the range of 4-11% of the Polywax as shown in Table 115. This is the most significant number for considering Kraton's effect on the properties of an explosive composition. With 2.3% Ganex WP-660, Kraton improved the stability of Polywax 600 from <1 minute to about 3 minutes.

TABLE 115. IMPROVED STABILITY OF POLYWAX TNT EMULSIONS

Emulsifier % of Polywax	Polywax No.	Kraton D1101 % of Ganex + Kraton	Kraton % of Polywax	Emulsion Stability Minutes Stable
20.7	600	-----	0	<1
"	"	7.4	1.6	<1
"	"	15.2	3.7	10
"	"	21	5.8	15
16	500	-----	0	<1
"	"	23	3.0	<1
"	"	30	6.9	20
"	"	40	10.7	20-30
2.3	600	-----	0	<1
"	"	5.3	0.6	1-2
"	"	11	1.2	1-2
"	"	16	1.8	3
"	"	21	2.6	3

In the above evaluations, Kraton was added last, incrementally, mixed and stability measured. When the test tubes containing the highest levels of Kraton were removed from the 90°C water bath, the contents solidified so quickly, they could not be cast. The Kraton is effective at considerably less than the maximum concentration in these evaluations. Compromise on viscosity probably favors Polywax 500 over Polywax 600. The fire retardant phosphate ester, Santicizer 148, would reduce viscosity considerably as discussed in regard to Tables 61 and 62 in Section VI. Other Kraton rubbers are available which would give less viscosity increase. Kraton with Ganex V-216 was ineffective in emulsifying Polywax 600 in molten TNT.

Cross sections of several explosive formulations have been examined by scanning electron microscopy (SEM). The first formulation consisted of 73.3% TNT, 24.4% Indramic 800 with 2.3 % Ganex WP-660. For comparison the second formulation contained 75% TNT and 25% Composition D2 (D2) (84% wax, 14% nitrocellulose and 2% lecithin). Figure 40 and 41 show top views of castings of these two formulations respectively.

Both explosives show a fairly uniform surface. The wax is blended well in both formulations and is not apparent in the microphotographs. Cross sections of these two compositions are shown in the following figures.

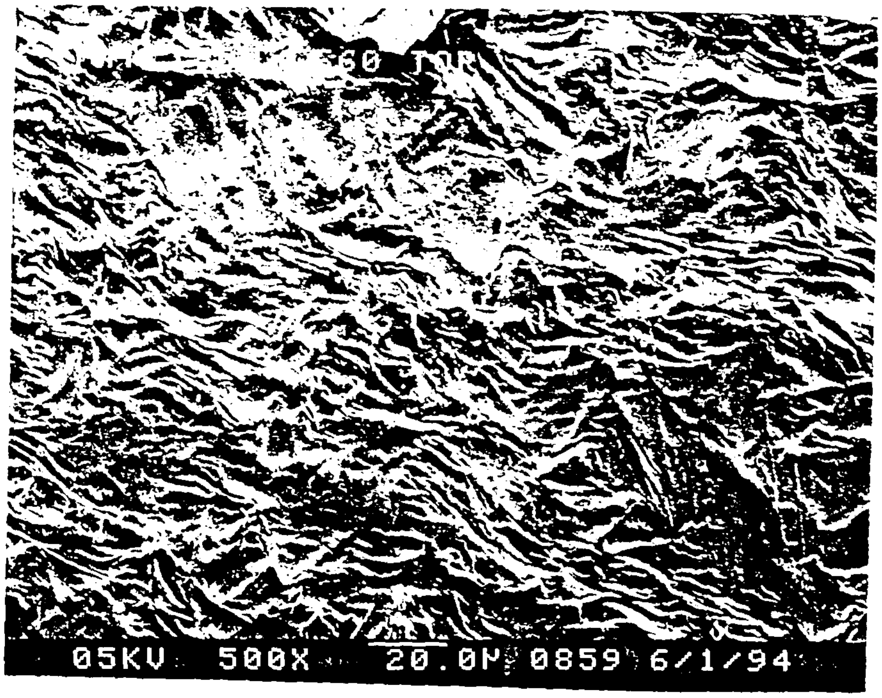


Figure 40. Top View Of TNT And Indramic 800 With Ganex WP-660 (500X)

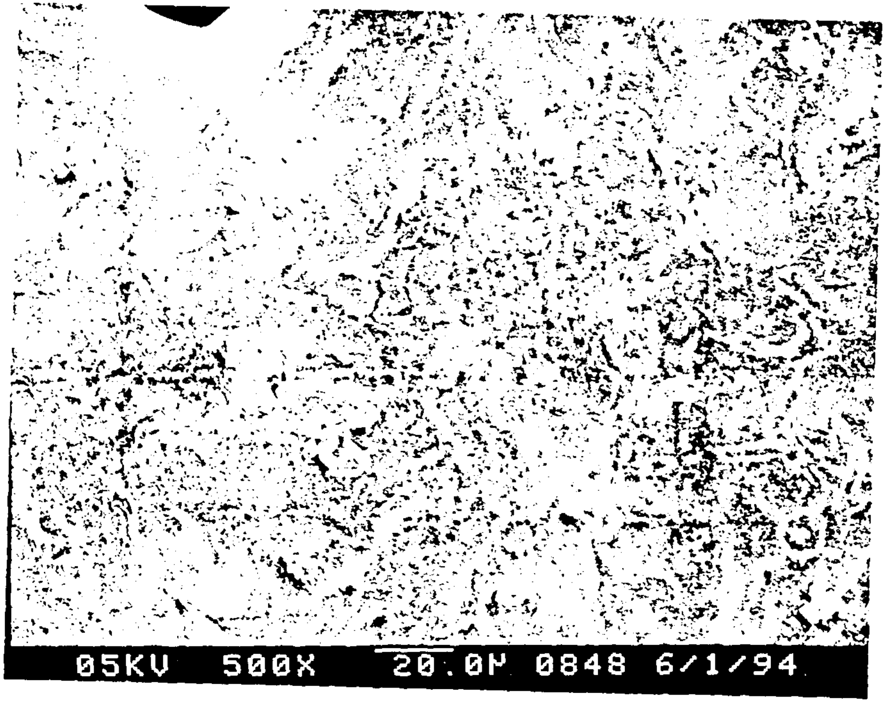


Figure 41. Top View Of TNT And D2 (500X)

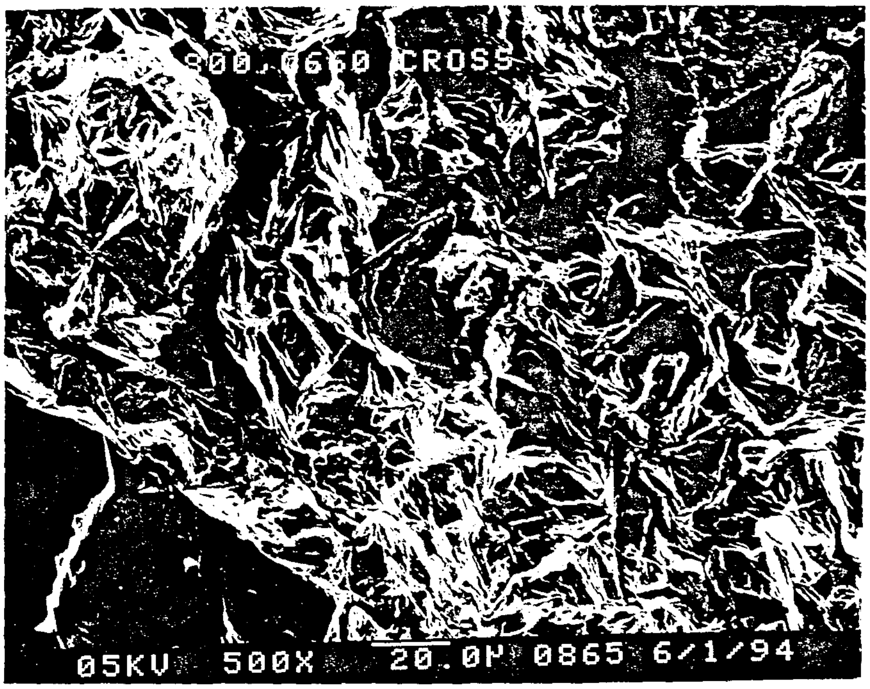


Figure 42. Cross Section Of TNT And Indramic 800 With Ganex WP-660 (500X)

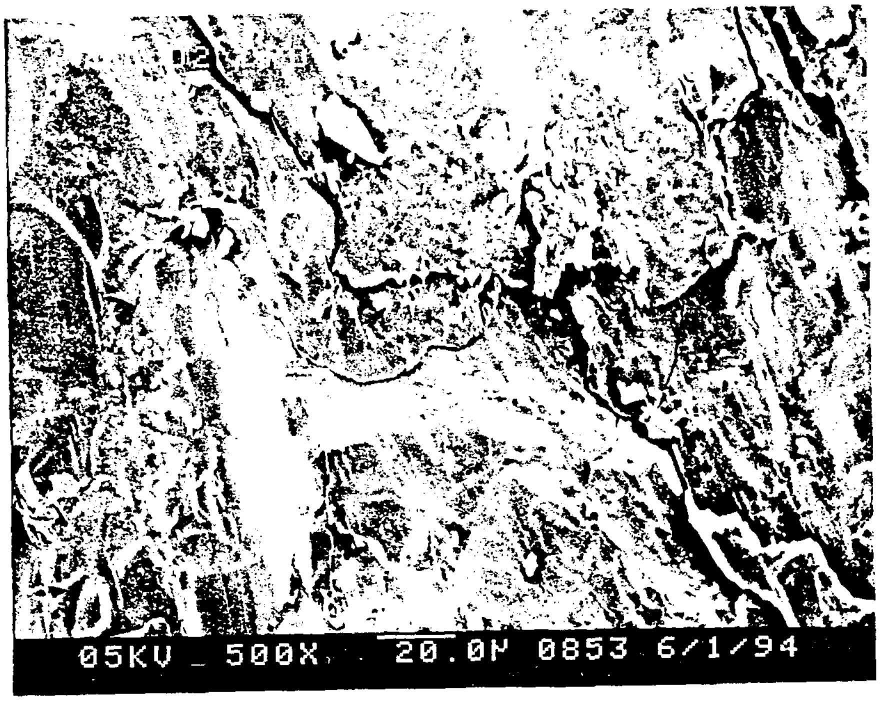


Figure 43. Cross Section Of TNT And D2 (500X)

Again the composition containing Ganex WP-660 appears fairly uniform, while the composition with TNT and D2 shows white strands of nitrocellulose which do not blend into the remaining components. The TNT and D2 also shows more fractures due to sectioning indicating a more brittle compositions.

The next explosive consisted of a mixture of 75% Octol, 20% aluminum, 4.85% wax and 0.15% Ganex WP-660 (APET 2). For comparison a composition was made which contained the same content of Octol and aluminum with 4.7% wax and 0.3% lecithin (APET 2A). Octol is a 75/25 mixture of HMX/TNT. An explosive without emulsifier was prepared but was too poor in quality to section and get microphotographs. Figure 44 and 45 shows cross sections of these two explosives at 100 magnification.

The HMX is seen as the textured structures embedded in the smoother matrix of the remaining constituents. With the composition containing Ganex resin, the section shows the HMX broken flush with the matrix due to the sectioning. With the lecithin emulsifier, the HMX granules show that sectioning has resulted in the dislodging of a portion of the HMX granule from the matrix. This dislodging indicates that the lecithin does not promote good wetting and good adhesion of matrix and HMX as the Ganex resin does. All of the HMX granules in the photograph of APET 2A show this dislodging to some degree. Figure 46 shows a magnification of the HMX granule in the upper left corner of Figure 45.

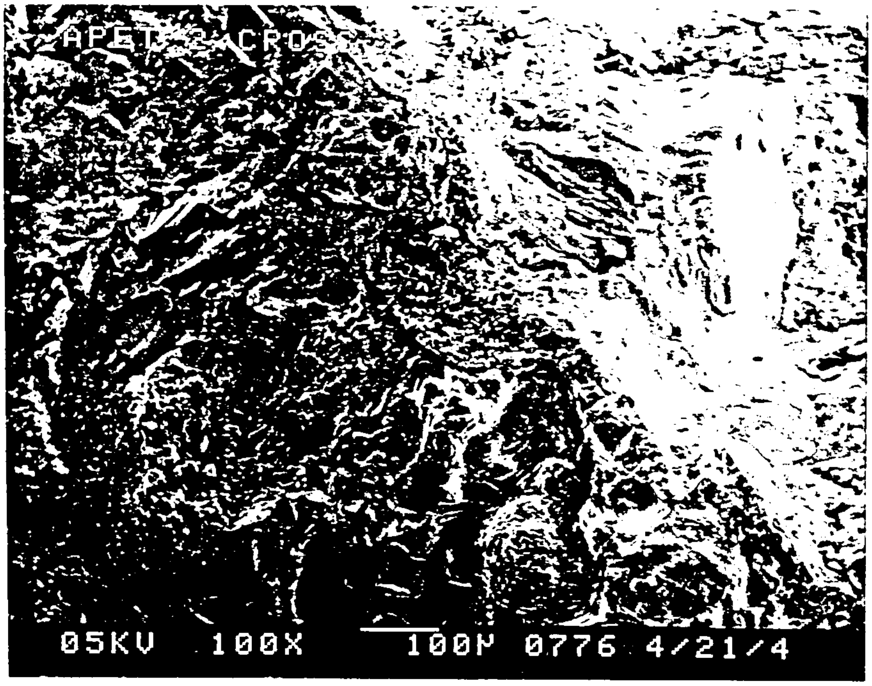


Figure 44. Cross Section Of Explosive Containing Ganex Resin Emulsifier (100X)

Figure 45. Cross Section Of Explosive Containing Lecithin Emulsifier (100X)

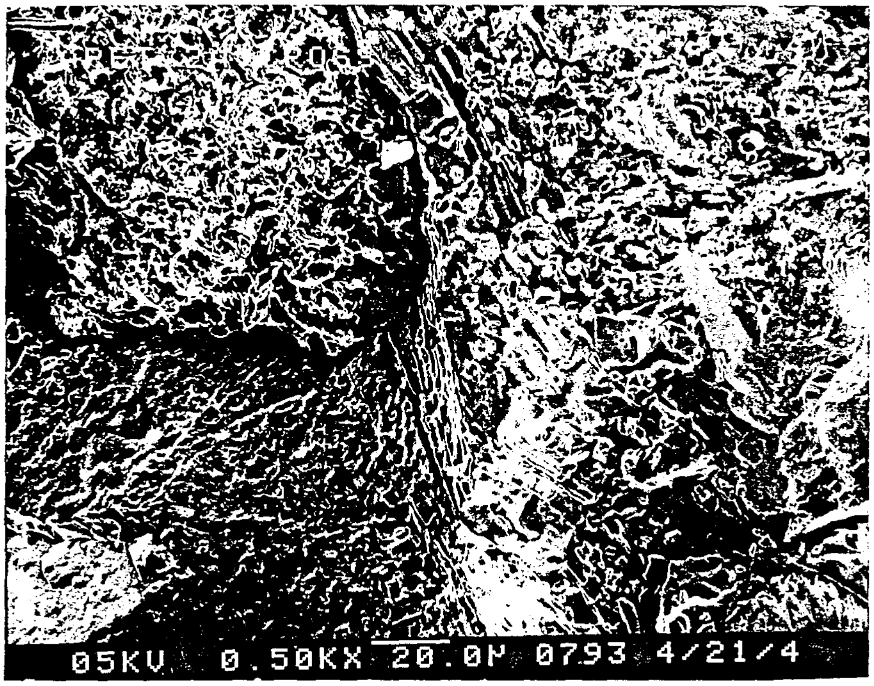


Figure 46. HMX Granule and Cavity In Explosive Containing Lecithin Emulsifier (500X)

The cavity walls from which a portion of the granule was dislodged are fairly smooth and uniform indicating that the matrix did not wet the HMX well. This poor wetting results in loss of adhesion when the matrix solidifies and allows portions of the granule to be more easy dislodged under the force of the sectioning process. Figure 47 shows a magnification of the HMX granule in the middle of Figure 44 in the explosive containing Ganex WP-660.

Sectioning of this explosive has resulted in some separation at the HMX matrix interface but there is no further suggestion of adhesive failure and in fact at the lower right of the granule the adhesion between matrix and granule is still intact.

Figure 48 shows what may be an aggregate of aluminum flakes in the explosive containing the lecithin emulsifier. Again the wetting and coating of the aggregate with matrix is seen to be poor.

Figure 49 shows the matrix of the explosive containing Ganex emulsifier which appears to be uniform.

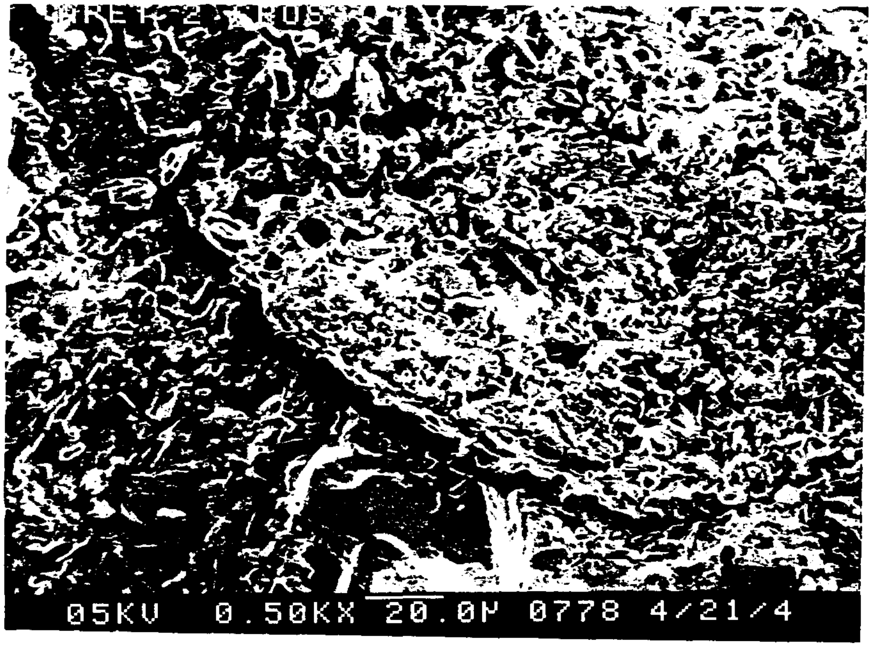


Figure 47. HMX Granule In Explosive Containing Ganex Resin Emulsifier (500X)

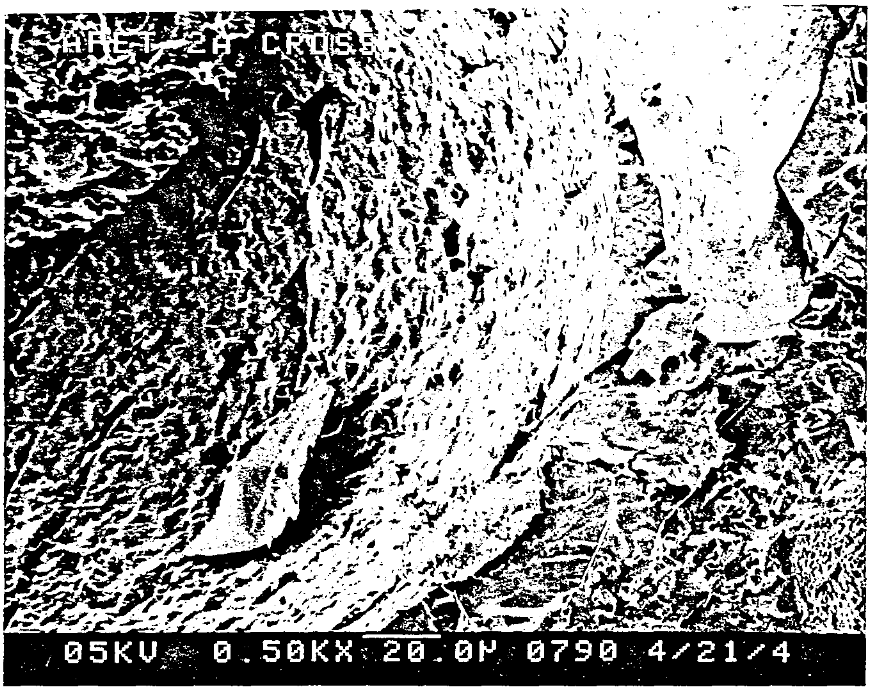


Figure 48. Aggregate In Explosive Containing Lecithin Emulsifier (500X)

Figure 49. Matrix of Explosive Containing Ganex Resin (500X)

5. CONCLUSIONS

A good emulsifier was found for the synthetic polyethylene wax, Polywax 600. Thus the technical objective was achieved. However, it is not as easy to emulsify Polywax 600 as the polar wax substitutes.

Polywax 600 does not offer the flexibility and as much potential for performance improvement as do the polar wax substitutes, but it is less expensive than most, but not all of them.

A wide variety of hypotheses were used to select or synthesize surfactants for emulsifying Indramic 170C microcrystalline wax. In spite of great effort, an acceptable alternative to the Ganex resin emulsifiers could not be found. Thus, the technical objective of identifying a back-up emulsifier for this challenging wax was not achieved.

Ganex resin emulsifiers are unique and very effective. As a replacement for nitrocellulose and lecithin in Composition D-2, a Ganex WP-660 emulsifier solved several serious problems plaguing development of AFX-644. This composition, reformulated with the Ganex emulsifier, was scaled up to 500 pound bomb testing in August 1993.

Ganex in AFX-644 wets and disperses powdered aluminum and the explosive fillers, resulting in greatly reduced viscosity. The reduction in viscosity allows two choices. One is to shorten mixing and casting times to increase production rates. The other is to increase the solids loading for greater explosive power.

The wetting and reduced viscosity should result in better coating of the explosive particles with wax, hence greater desensitization. This may be the reason that the blast test of AFX-644 showed 60% less explosive power than expected based on results from the formulation using nitrocellulose in Composition D-2.

The following modifications may solve this problem:

- Use less wax.
Use higher solids loading
- Use Ganex V-216 instead of Ganex WP-660. Its different polarity may have a different effect on mechanisms responsible for desensitization.
- A combination of the foregoing adjustments probably offers the best chance of balancing the required desensitization against the blast power.

A ten-fold reduction in viscosity was obtained using 0.2% Ganex V-216 or V-220 in WL/MNME's modified AFX-931 PBX at Atlantic Research Corporation (Reference 29). (This work was done for MACH I outside the present contract.) A similar viscosity reduction may be achievable in AFX-644.

The Ganex resin family is unique in providing excellent wetting dispersing, coating and viscosity reduction in addition to being outstanding for emulsification. Other good dispersants that reduce viscosity significantly in AFX-931 and other high solids compositions, such as rocket propellants, are ineffective for emulsifying Indramic 170C wax and Polywax 600 in nitroethane.

The critical diameter of AFX-644 explosive containing a Ganex resin surfactant exhibited very unusual behavior that could have fundamental significance. No other surfactant has ever shown this.

Ganex resin emulsifiers are expected to be effective emulsifiers in most melt cast explosive formulations such as Compositions B, D-2, H-6, etc.

Ganex resin emulsifiers are expected to be effective dispersants and confer important benefits in batch or continuous mixing of many anhydrous explosives, propellants or pyrotechnics.

Optical photomicrographs of wax with 2,4-DNT (50°C MP) simulant confirm the stated benefits of Ganex resins in respect to wetting, coating and dispersion of wax on 2,4-DNT crystals, or emulsifying droplets in nitroethane or molten 2,4-DNT.

SEM photomicrographs demonstrate that as little as 0.15% Ganex WP-660 is far superior to 0.3% lecithin in an aluminized Octol (HMX/TNT) composition for emulsifying wax, filling voids, coating HMX crystals, and reinforcing the HMX crystal. This supports statements in this report that Ganex dispersants not only emulsify but also wet, disperse, reduce viscosity, fill voids and therefore should improve desensitization by wax.

SECTION VIII

MODIFY PRODUCT, IF NEEDED, TO CORRECT WL/MNME PROBLEMS

1. SUMMARY

The technical objective of Task 5 is to assist WL/MNME in overcoming any unforeseen performance problem beyond MACH I's responsibility for providing effective emulsifiers. This technical objective has been met in all instances.

WL/MNME found that casting AFX-644 using Lot 1001 of Ganex WP-660 resin gave lower density than the castings using Lots 1003 and 1004. Comparing lot analyses including that of MACH I's Lot 1002, moisture by difference was 1.7% for Lot 1001 compared to 0.5% for the other three lots. Discussion with the manufacturer (ISP) revealed that this was the first lot they had produced and some of it was vacuum-stripped of *n*-hexanol processing solvent and some was not. They analyzed WL/MNME's Lot 1001 and found 0.7% hexanol. This may or may not have caused low density. The manufacturing specification since production of Lot 1001 has been 0.03% hexanol maximum because of concern by other customers. Whatever the cause of the low density, it is not expected to recur due to quality of Ganex WP-660 resin.

MACH I had ISP synthesize a modified Ganex WP-660 resin by changing the polarity through a change in ratio of alkyl group to pyrrolidone ring, and alternatively providing Ganex WP-660 of altered molecular weight. This was in response to WL/MNME's apparent problems with critical diameter and gassing. These structural changes were intended to correct the apparent problems. Ganex WP-660 specimens of altered molecular weight produced stable emulsions of Indramic 170C wax in nitroethane but not in TNT or 2,4-DNT. The polarity modifications did not result in stable emulsions with nitroethane. The apparent problems with Ganex resin proved to be spurious, so no corrective action was actually required.

In a meeting with WL/MNME MACH I suggested that a frothing problem, attributed by some to gassing provoked by Ganex resin surfactant, was probably due to mixing technique and that air was being beaten into the mix. The next mix was conducted using modified technique; it produced good castings with density close to theoretical and no indication of froth. Subsequent castings have also been good.

By a phone inquiry on April 26, 1994 MACH I found that in a blast test WL/MNME had just measured 60% lower explosive power with AFX-644 than expected. Ganex resin surfactants are excellent wetting and dispersing agents as well as emulsifiers. This should result in lower viscosity in AFX-644 and a better wax coating of particles. This implies exceptional desensitization and provides a basis for several formulation adjustments to correct the problem. WL/MNME is optimizing AFX-644 to correct the problem.

2. DISCUSSION

Ganex surfactant in AFX-644 should wet and disperse aluminum and the explosive fillers resulting in a large reduction in viscosity. The viscosity reduction presents two options. One is to shorten mixing and casting time and thereby increase production rate. The other is to increase solids loading for greater explosive power.

The wetting and reduced viscosity should result in better coating of the explosive particles with wax, hence greater desensitization. This is probably the reason that the blast test of AFX-644 showed 60% less explosive power than expected based on results from the formulation using NC in Composition D-2.

Several modifications would be expected to correct the problem.

- Use less wax
- Use more fillers
- Substitute Ganex V-216 for Ganex WP-660. Its different polarity may have a different effect on some of the mechanisms affecting desensitization.

A combination of these adjustments probably offers the best chance of balancing the required desensitizing without losing the blast power.

SECTION IX

PHASE III COMMERCIALIZATION AND TECHNOLOGY TRANSFER PLANS

1. TECHNICAL OBJECTIVES

The overall objective of Task 6 is to develop plans for Phase III commercialization. This has been done. A supportive effort for the achievement of this objective is to develop patentable technology. The use of Kraton D1101 with Ganex WP-660 to achieve a stable emulsion of Polywax 600 with TNT is believed to be patentable as an extension of the patent application already submitted teaching the use of Ganex surfactants as emulsifiers for wax in TNT. Another supportive activity is to explore and recommend methods to transfer technology to the private or public sector. This also has been done.

2. SURFACTANTS

The three alkyl polyvinylpyrrolidone resins produced and sold by International Specialties Products, Inc. (ISP) are uniquely excellent wax emulsifiers for TNT melt cast bomb explosives such as AFX-644. These surfactants are Ganex V-216, V-220 and WP-660 resins. They also have been demonstrated to perform other very important functions such as improving wetting, coating and dispersing of explosive fillers such as RDX, NTO, HMX, ammonium perchlorate and aluminum. This reduces viscosity significantly and can either speed up production by reducing mixing and casting time, or can allow higher solids loading. With better wetting and coating, wax desensitizers will be more effective.

The unique Ganex resin surfactants have also been demonstrated to reduce viscosity ten-fold in processing of a modified AFX-931 PBX explosive, increasing production rate or allowing higher solids loading. The modified AFX-931 contained 15% aluminum, 32% RDX, and 37% ammonium perchlorate. The viscosity-reducing capability of Ganex surfactants should be applicable and beneficial as a processing aid for many munitions mixing processes. Solid rocket propellant mixes consisting of similar energetic, oxidizer and fuel compontents should show similar rheological improvements from this technology. Products that might benefit include ammunition, bombs, missiles, mines, projectiles, pyrotechnics, demolition charges, and special purpose devices.

Ganex surfactants are expected to serve as improved emulsifiers for Compositions such as B, D-5, HBX-1 and H-6.

3. PETROLEUM WAXES

The variations in composition and performance of petroleum waxes has posed serious problems for decades. MACH I has identified a glc analytical method, more sensitive than any other available, that can detect changes in composition immediately.

4. WAX SUBSTITUTES

MACH I has identified synthetic chemicals and polymers that are expected to desensitize as well as, or better than, petroleum waxes. Moreover, supplies and quality of these synthetic materials are expected to be dependable for the indefinite future. These desensitizers have been selected to operate by varying mechanisms to permit tailoring explosives for different applications such as artillery projectiles versus bombs. Having this choice of mechanisms could be crucial in mitigating fuzing problems or minimize loss of blast power with a desensitized composition. The Ganex resin surfactants are needed to emulsify these desensitizers in TNT melt-cast explosives.

5. COMMERCIALIZATION AND TECHNOLOGY TRANSFER PLANS

With the approval and support of WL/MNME, MACH I plans to vigorously inform the various branches of the U.S. Department of Defense and its primary energetic contractors such as Atlantic Research Corp. (Sequa), Thiokol Corp., United Technologies Corp., Hercules and Aerojet-General Corp. of the merits of Ganex surfactants for many aerospace and explosive applications.

MACH I, Inc. and ISP have agreed to a joint effort to extend the SBIR Phase II development into a Phase III business effort. ISP technologies Inc. (formerly GAF) will produce Ganex and Antaron alkylated pyrrolidone resins. MACH I, Inc. has an exclusive global right to promote and develop sales for these products within the U.S. Standard Industrial Code ("SIC") 2892, Explosives, Pyrotechnics and Propellants. The Ganex resins will be marketed and serviced within this SIC Code by MACH I, Inc. The Ganex resins will be added to the MACH I, Inc. military/ aerospace chemicals product line (Appendix L).

A paper on the successful use of Ganex resin surfactants to emulsify desensitizing wax in the TNT melt cast system was presented to the Explosives and Propellants Subgroup Meeting at the Holston Army Ammunition Plant on August 25, 1993. This developed considerable interest. As a result of this paper, ARDEC at Picatinny Arsenal was sampled with Ganex resin surfactants and MACH I made some suggestions on their use in formulations. Picatinny has a new world class micro-factory with state-of-the-art processing equipment to support IM propellant and explosive studies. They will use a twin screw mixer/extruder for processing. MACH I will offer assistance to ARDEC in this significant operation. NSWC at Indian Head, Maryland also requested GANEX samples to replace lecithin in a new IM explosive formulation they are developing. MACH I will also follow up on this.

MACH I presented a paper "Viscosity Reducing Dispersants for Plastic-Bonded Explosives" at the 1993 JANNAF PROPULSION MEETING in Monterey, California on November 16, 1993. Two Ganex resin surfactants and other surfactants reduced the viscosity of a modified AFX-931 PBX bomb mix ten-fold.

Mining, road building, quarries and building site preparation consume large quantities of explosives. MACH I personnel have developed and sold products including surfactants to these industries and so are familiar with them.

Several groups have meetings or journals that are pertinent to civilian markets. They will be considered for presentations, publications, or attendance to make suitable contacts. The International Pyrotechnics Society has their annual meeting this July 1994 in Colorado Springs. Their following meeting will be September 1996 at Moscow, Russia. The International Society of Explosive Engineers has their annual conference on Explosives and Blasting Technique and Research Symposium on February 2-6, 1995. They also publish the journal of Explosive Engineering. Explosive and Pyrotechnics Newsletter conducts a Symposium periodically; the next will probably be in about eighteen months.

6. TECHNOLOGY TRANSFER PLANS

Ganex Resins are not listed in the Department of State Bureau of Politics - Military Affairs 22 CFR Part 120 et al. Amendments to the International Traffic in Arms Regulations; Final Rule dated July 22, 1993. On the other hand, as a result of this research effort a control status determination regarding Ganex resins should be made prior to an extensive international sales effort for these products.

MACH I, Inc. will establish through Department of State Communication whether or not Ganex Resin should be included on the U.S. Munitions List. In as much as surfactant processing aids such as lecithin are not so listed, it is the opinion of MACH I, Inc. that Ganex Resins should also be exempted from Department of State licensing control. However, this must be determined officially by responsible officials of the U.S. Government.

SECTION X

CONCLUSIONS

MACH I has developed a good emulsifier for Polywax 600 in nitroethane by adding 10-15% of a styrene-butadiene block copolymer coupling agent to Ganex WP-660. Ten minutes emulsion stability was obtained. WL/MNME confirmed this with molten TNT using 20% emulsifier based on wax (the level in Composition D-2 and that used at MACH I). Emulsion stability (miscibility) of 15 to 20 minutes was achieved in three tests by WL/MNME.

Despite exhaustive testing of many surfactants, including many specially synthesized amine salts and esters, the only emulsifiers found to be effective for Indramic 170C microcrystalline petroleum wax in nitroethane, 2,4-DNT and TNT are the Ganex resin family of three alkyl polyvinylpyrrolidone resins.

Besides uniquely effective emulsification the Ganex resin surfactants provide these additional important benefits:

- Better wetting of particles
- Better dispersion of particles
- Better coating of particles
- Reduced friction
- Reduced viscosity
- Reduced entrapment of air, which raises density
- Increased desensitization
- Increased production rate for TNT melt casting and PBX.

Optical photomicrographs have been taken of a number of emulsions of wax in simulant (nitroethane and 2,4-DNT) with and without Ganex emulsifier. The photomicrographs confirm the stated benefits of Ganex in respect to wetting, coating, and dispersion of wax on 2,4-DNT crystals or emulsified droplets in nitroethane or molten 2,4-DNT.

SEM photomicrographs show that 2.3% Ganex WP-660 substituted for 4.0% nitrocellulose plus lecithin in a 75% TNT and 25% Composition D-2 explosive casting greatly reduced brittleness as evidenced by fracture lines created in sectioning the casting for SEM. Composition D-2 consists of 84% wax, 14% nitrocellulose and 2% lecithin. This verifies the very valuable ancillary benefits of the Ganex resin emulsifiers.

SEM photomicrographs also demonstrate that as little as 0.15% Ganex WP-660 greatly outperforms 0.3% lecithin in an aluminized Octol (HMX/TNT) composition by emulsifying the wax, coating the HMX crystals, strengthening HMX crystals, and filling voids. The Ganex casting also appeared better to the unaided eye than the lecithin casting. This confirms the special benefits cited above.

Using only 0.2% Ganex V-216 or Ganex V-220, Atlantic Research Corporation achieved a ten-fold reduction in viscosity of modified AFX-931 general purpose PBX bomb explosive. Both mixes processed so well that the two-hour holding period usually necessary to obtain a castable mix could be eliminated. The formulation contained ammonium perchlorate, RDX and aluminum powder. This work was done for MACH I outside the present contract.

As a replacement for nitrocellulose and lecithin in Composition D-2, Ganex WP-660 has solved many serious problems plaguing the development of AFX-644. Development of reformulated AFX-644 containing Ganex WP-660 progressed to testing of 500 pound bombs about 10 months ago. Optimization for potential production is underway.

The critical diameter of Ganex WP-660 bomb compositions exhibited very unusual behavior that could have fundamental significance.

Various mechanisms for desensitizing TNT were emphasized in selecting candidate wax substitutes. Ganex resin emulsifiers or co-emulsifiers provided good emulsion stability with nitroethane for sixteen candidates that were then evaluated by WL/MNME for DSC compatibility and emulsion stability with TNT. Eleven were considered acceptable although only about 2.5% of Ganex WP-660 based on wax was used instead of the 20% emulsifier used in Composition D-2 and at MACH I with TNT simulant evaluations.

The polar wax substitutes range from liquids to solids melting up to a maximum of 100°C, with a few exceptions such as Kraton D1101. Polar wax substitutes are expected to wet, coat, and disperse explosive fillers more easily and completely than wax. These are important mechanisms in desensitization. Lower-melting or liquid polar wax substitutes with lower viscosity are expected to wet, coat, disperse, and fill voids in the explosive particles even more quickly and completely. All these factors promote desensitization and increase production rate by shortening mixing and casting time. Polar desensitizers may be less subject to exudation because they may dissolve in TNT or bond to particulates. Wax substitutes that desensitize by different mechanisms are very important for developing explosives intended for differing applications such as shells and bombs. If a desensitized explosive proves to be insensitive to the fuze or gives too little explosive power, replacing the wax substitute with one desensitizing by a different mechanism may solve the problem. The replacement could be used alone or blended with a wax such as Indramic 800 or Polywax 600.

The wax substitutes offer much greater flexibility than microcrystalline petroleum wax or synthetic hydrocarbon waxes such as Polywax 600. In contrast to petroleum wax, they are available in ample quantity and consistent quality for the indefinite future. Moreover, they are easier to emulsify.

The polar wax substitutes cost $0.46 to $3.29/lb. compared to $1.19 for Polywax 600 and $0.90 for Indramic 800. The naphthenic process oil Telura 343 costs only $1.50/gal. The possibly higher cost of some of the substitutes may be justified by the potential improvements in performance discussed above.

With microcrystalline petroleum waxes like Indramic 800, Polywax 600 or wax substitutes the Ganex resin emulsifiers/dispersants are expected to be generally effective in melt cast systems such as Compositions B, HBX-1, D-2, and H-6.

Ganex additives should also be generally effective in reducing viscosity of PBX compositions such as AFX-931, in batch mixing, or continuous mixer/twin screw extruder processing. They appear promising for use in many anhydrous munitions mixing processes used to manufacture ammunition, bombs, missiles, projectiles, pyrotechnics, demolition charges, and special purpose devices.

SECTION XI

RECOMMENDATIONS

DOD should build on the achievements of the present work by establishing a program to:

- Exploit more fully the following important benefits offered by top quality emulsifiers, such as the Ganex resin family:
    - Better wetting
    - Better dispersion
    - Reduced viscosity
    - Nonexplosive classification
- Replace today's undependable and inconsistent desensitizing wax with synthetic substitutes that offer:
    - Superior desensitization
    - Improved physical stability of finished explosive
    - Dependable, controlled properties
    - Assured availability

The program should include appropriate application of the superior emulsifiers and wax substitutes to:

- All melt-cast explosive systems such as Compositions B, HBX-1, D-2, and H-6
- Batch- and continuously-mixed PBX systems
- Other anhydrous munitions mixing processes, including those for manufacture of ammunition, bombs, missiles, projectiles, pyrotechnics, demolition charges, and special purpose devices.

The program should investigate the fundamental mechanisms associated with GANEX resin effectiveness in desensitizing energetic systems. The present work clearly identified the GANEX utility in this regard, but also indicated formulation constraints relevant to use concentration effectiveness. When the fundamental model of GANEX resin performance is understood, the unique contribution of additive levels of this to various energetic systems could be optimized. A new control mechanism for formulating and compatabilizing a wide variety of explosives, propellants, and pyrotechnics would hence be available.

MACH I, Inc. has demonstrated the qualification to serve as contractor for such a program and to transfer the related technology to the public and private sectors. Beyond the technology generated under the present program, MACH I has:

- Extensive expertise in the field of surfactants.
- Experience in the field of energetic compositions (explosives, propellants, pyrotechnics).
- Outstanding marketing capabilities for promoting innovative concepts and products.
- A strong commitment to sell the technology and *M*ilitary *A*erospace *CH*emical *I*ngredients.

MACH I recommends and has requested WL/MNME assistance during its SBIR Phase III Commercialization efforts by preparing a paper for publication and joint presentation with MACH I which details WL/MNME work and research and development conclusions on the utility of Ganex resins in TNT based bomb desensitizing formulations. Targeted audiences for these presentations include:

- Present a short paper to the Explosives and Propellants Subgroup Meeting as was done at the meeting at Holston Army Ammunition Plant on August 25, 1993.
- Present a paper at a JANNAF Interagency Propulsion Commitee Meeting on the subject of manufacturing technology for insensitive munitions (IM), propellants and explosives
- ADPA Meeting in 1995.
- ICT Annual Conference in 1995.

APPENDICES

APPENDIX A

INTERNATIONAL SPECIALTY PRODUCTS

APPENDIX A
INTERNATIONAL SPECIALTY PRODUCTS

INTERNATIONAL SPECIALTY PRODUCTS

PO Box 1006 Bound Brook NJ 08805

Tel: (908) 271 9504
Tel: (800) 541 3497
Fax: (908) 356 6710

Effective: April 1, 1994

PRICE SCHEDULE

GANEX® ALKYLATED VINYL PYRROLIDONE POLYMERS

PRICE PER POUND

PRODUCT	DRUMS C/L, T/L	DRUMS 20-T/L	DRUMS 1 - 19	DRUM FILLING WT. (#)	PACKAGE 50 LBS.	PACKAGE 8 LBS.
GANEX V-216	$ 9.54	$ 9.64	$ 9.74	400	$10.04	$11.74
GANEX V-220	10.26	10.36	10.46	400	10.76	12.46
GANEX V-516 (55% IN IPA)	4.06	4.16	4.26	400	4.56	6.26
GANEX P-904 (100% PDR.)	18.52	18.62	18.72	100	--	20.72
GANEX P-904 (45% IN IPA)	9.70	9.80	9.90	400	10.20	11.90
GANEX P-904 (45% IN NMP)	9.70	9.80	9.90	400	10.20	11.90
					25 LBS.	4 LBS.
GANEX WP-660	9.93	10.03	10.13	200	10.43	12.13

TERMS: Prices are FOB Calvert City, KY. All shipments from ISP Warehouses are FOB Ex Warehouse, plus branch upcharge as follows:

$0.04	Charlotte, NC	$0.08	Santa Fe Springs, CA
$0.04	Chicago, IL	$0.05	Texas City, TX
$0.04	Farmingdale, NJ		

In the event that product inventory is not available from an ISP Warehouse, shipment will be priced FOB Calvert City, KY.

NET 30 DAYS.

PRICES ARE SUBJECT TO CHANGE WITHOUT PRIOR NOTICE.

Ganex Structure and Properties

The Ganex structure is shown on the following page. The increasing alkyl chain length of Ganex V-216, V-220 and WP-660 results in increasing hydrophobic properties as characterized by an HLB number of 10, 8 and 6 respectively. Ganex properties are shown on the page following the structure.

The decomposition temperatures are 349, 336 and 350°C respectively as shown on the (TGA) curves for Ganex V-216 following the properties table.

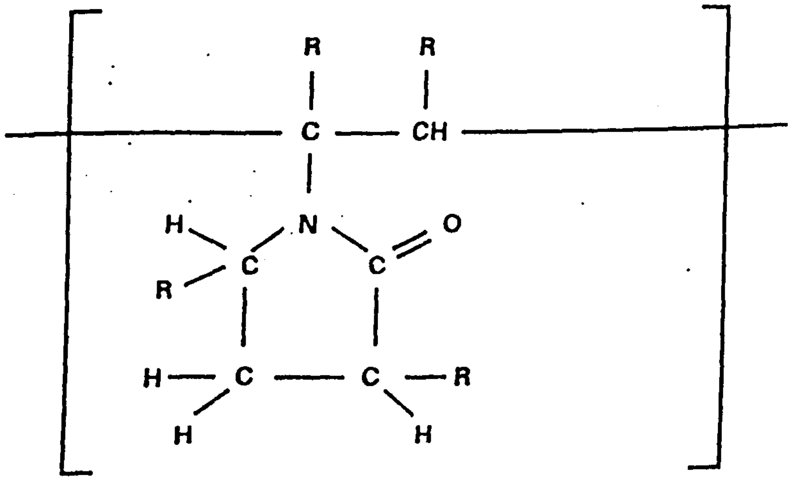
ISP has found that carboxylic acids react with polyvinylpyrrolidones by forming a complex with the carbonyl group (shown by an infrared spectra shift of the carbonyl absorption). If molten TNT reacts with Ganex, it would probably also be through the carbonyl group.

GANEX STRUCTURE

II. Chemistry

GANEX® polymers are derived from vinylpyrrolidone and long chain alpha olefins. By controlling the molecular weight, alkyl chain length and degree of alkylation, performance can be built into the molecule. Structurally, GANEX® alkylated polyvinylpyrrolidones can be represented as:

Figure 1
Structure of GANEX® Resins



with R representing either an alkyl group or a hydrogen.

GANEX PROPERTIES

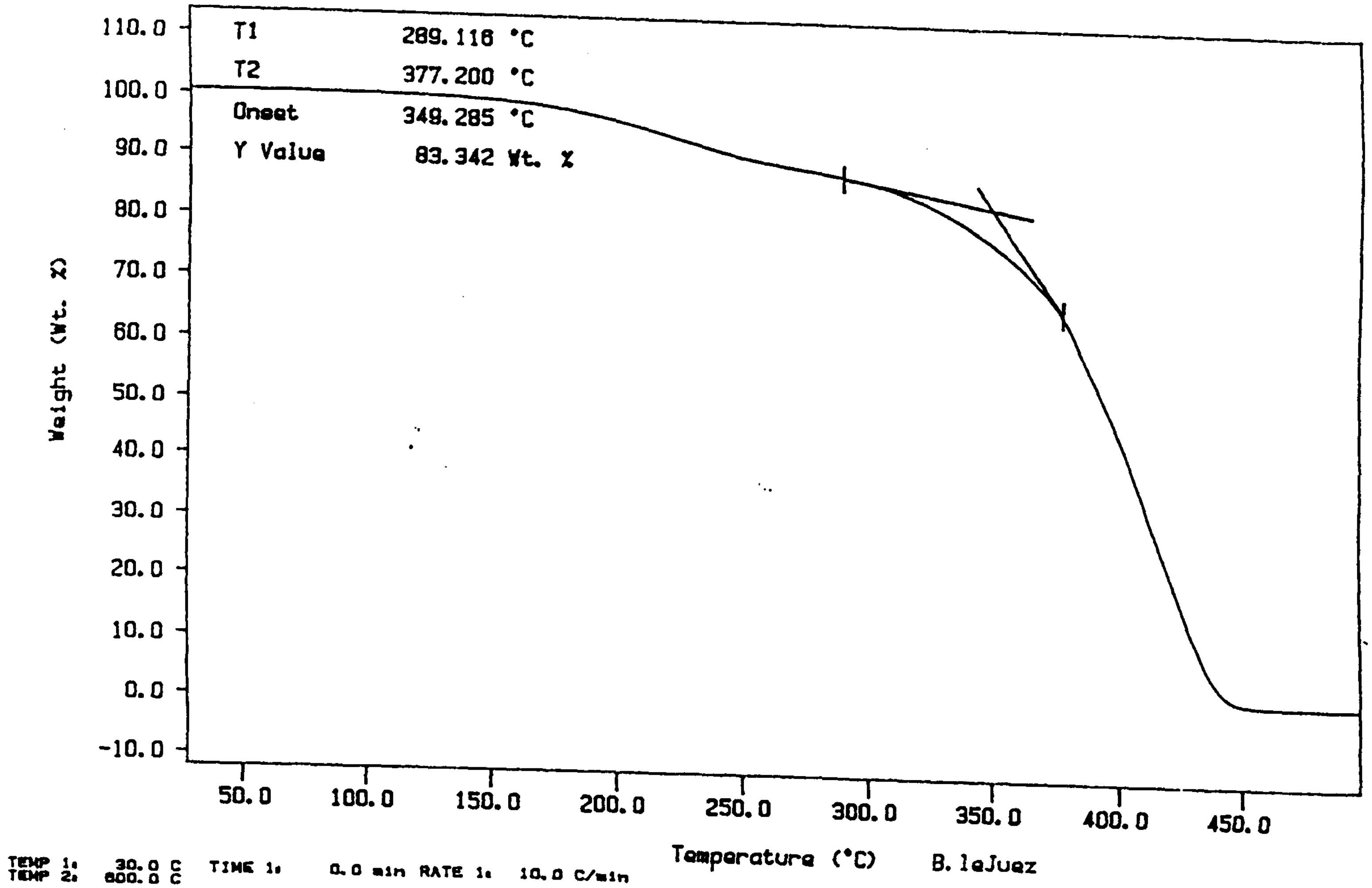
TYPICAL PROPERTIES OF GANEX$^{(R)}$ RESINS

	GANEX$^{(R)}$ V-216 Polymer	GANEX$^{(R)}$ V-220 Polymer	GANEX$^{(R)}$ WP-660 Polymer
CTFA Designation	PVP/Hexadecene Copolymer	PVP/Eicosene Copolymer	Tricontanyl PVP Copolymer
Physical Form	liquid	solid	solid
% Activity	100	100	100
Appearance @ 25 C	pale yellow viscous fluid	off white waxy solid	off white flakes
Solidification Point	---	35-40 C	60 C
% Nitrogen	2.0 - 3.0	2.9 - 3.6	2.0 - 3.0
HLB requirement	10	8	6
Solubilities*:			
Kerosene	S	S	
Mineral Oil	S	S	S
Castor Oil	S (5%)	I	
Ethanol	PS	I	I
n-propanol	I	I	I
Water	I	I	I

*S = Soluble to 20% GANEX$^{(R)}$, except as noted
PS = Partially Soluble
I = Insoluble

TGA File Name: sk900
Sample Weight: 21.670 mg
Fri Jul 30 13:54:07 1993
Ganex V-216 in N2

PERKIN-ELMER
7 Series Thermal Analysis System



Typical Pigment Dispersions

In Ultracene

Pigment	Ganex® V-216			Ganex® V-220			Competitive Polymeric Dispersant		
	Optimum Conc.	% Pig. Solids	BKFLD Vis (Cps)	Optimum Conc.	% Pig. Solids	BKFLD Vis (Cps)	Optimum Conc.	% Pig. Solids	BKFLD Vis (Cps)
Zinc Oxide (Photox 801, N. J. Zinc)	4.0	70	240	4.0	70	300	1.5	70	850
		80	750		80	1,000		75	1,850
		85	1,500		85	1,600		80	4,000
								85	Off Scale
$CaCO_3$ (Purecol O, BASF-Wyandotte)	4.0	50	18	3.0	50	32	2.0	50	150
		60	200		60	250		60	300
		70	500		70	1,250		70	1,400
		75	1,400		75	1,750			
					80	8,500			
TiO_2 (R-755, N. J. Zinc)	6.0	50	13	6.0	50	10	5.0	50	300
		60	250		60	38		60	1,450
		70	1,500		70	150		70	6,000
		75	5,000		75	500		75	37,500
		80	16,250		80	2,900			
Red Iron Oxide	4.5	50	13	4.5	50	13	4.5	50	75
		60	237		60	250		55	1,250
		70	1,350		70	1,500		60	4,000
		75	3,000		75	5,000		65	8,250
		80	8,750		80	16,250		70	14,750
		85	25,000					75	42,500
Yellow Iron Oxide	10.0	50	100	9.0	50	63	4.0	50	1,750
		55	125		55	175		55	3,500
		60	300		60	350		60	5,000
		65	700		65	1,150		65	7,500
		70	3,600						
Chrome Yellow	2.5	50	43	2.5	50	63	3.0	50	60
		60	250		60	325		60	350
		70	1,200		70	1,750		70	4,550
		80	4,500		80	8,500		80	27,000
Phthalocyanine Green Toner 66-3001 (GAF)	11.0	50	200	9.0	50	180	6.0	45	80
		55	2,750		55	2,000		50	600
		60	33,750		60	48,000		55	4,000
Phthalocyanine Blue Toner 56-6001 (GAF)	13.0	40	350	8.0	40	150	6.0	35	50
		45	3,750		45	1,250		40	200
		50	17,500		50	13,000		45	1,200
Carbon Black (Elftex S, Cabot)	10.0	20	1,500	5.0	20	3,000		Ineffective	
		25	8,000		25	Off Scale			
		30	33,000						

Pigment Dispersion

GANEX® V-216 and GANEX® V-220 polymers function as dispersants for many of the pigments used in colored cosmetics. In aliphatic vehicles, typical use levels range from 2.5% to 0.9% GANEX® resin based on the weight of pigment.

The typical concentrations, and appropriate GANEX® polymer, for various cosmetic pigments are shown in Table 2. Since the pigment dispersions would be further compounded in developing formulated products, the actual levels of GANEX® polymer would be much lower. Additional GANEX® may be incorporated into the oil phase of an emulsion system or anhydrous base to provide water and wear resistance.

Table 2
Pigment Dispersion Guide

Pigment:	GANEX® Polymer	Typical use level
Titanium Dioxide	V-216 or V-220	6.0%
Zinc Oxide	V-220	4.5%
Iron Oxide, Yellow	V-220	9.0%
Iron Oxide, Red	V-216 or V-220	4.5%

The use of GANEX® polymers as pigment dispersants will help to improve the pigment efficiency and provide better coverage from make-up systems.

Stick Integrity

The GANEX® polymers will improve the integrity of stick products such as eye pencils, cover sticks and lip care products. In the past, this had been accomplished by the addition of more waxes, often resulting in a stick which is difficult to apply. GANEX® polymers allow the formulation of sticks that are firm yet spread smoothly and easily. The selection of the best GANEX® polymer will depend on the performance requirements of the system under development. For example, GANEX® V-216 resin is a better choice for the system in Table 3 for improving stick hardness as indicated by a lower penetrometer reading.

Table 3
Effect of GANEX® Polymers on Lipstick Bases

	Wt. %		
	1	2	3
GANEX® V-216	—	2.3	—
GANEX® V-220	—	—	2.3
Candelilla Wax	9.3	9.3	9.3
Carnauba	3.5	3.5	3.5
Beeswax	5.8	5.8	5.8
Glyceryl Dilaurate	3.5	3.5	3.5
Polyglyceryl-3-diisostearate	34.9	34.9	34.9
Lanolin Oil	23.3	23.3	23.3
Isocetyl Alcohol	11.6	11.6	11.6
Tridecylneopentanoate	8.1	5.8	5.8
Penetrometer reading*	105	92	107

* Average of 7 readings, after 24 hours equilibration at ambient temperature

In spite of the increased hardness, the stick containing GANEX® V-216 retained the excellent spreading characteristics which are desirable for lip care products. In eye and cheek pencils, this translates to easier sharpening while maintaining smooth application and excellent color blending.

APPENDIX B

IGI BOLER INCORPORATED

APPENDIX B
IGI BOLER INCORPORATED

COMMENTS ON G.C. ANALYSIS OF PETROLEUM WAXES

Although the general procedure for using gas chromatography for analysis of paraffin waxes has been in use for over 30 years, particularly by the petroleum refining and rubber industries, there is no ASTM caliber test procedure "on the books" at the present time (Circa Jan. 1990).

This is because the test results obtained reflect the resolution of the test equipment and the methods used for sample testing. The repeatability of most up-to-date G.C. analysis supports use of the data for a wide range of practical applications. The reproducibility of G.C. analysis of petroleum waxes across methods and equipment is so poor however that waxes cannot be evaluated nor specifications set. In other words, Observer A can use his own method for evaluating his own waxes or other waxes run by his method. He cannot, however, judge the character of his own or other waxes if the test data comes from different equipment and test procedures supplied by Observer B.

On-going work within ASTM to develop a consensus method providing usable repeatability and reproducibility factors has not been encouraging. The situation is further complicated by continuous improvement in equipment and a reluctance on the part of long time users to abandon their data banks and start 'new' with an unknown consensus procedure.

It is the current policy of IGI BOLER, INC. to provide typical G.C. analytical data for standard grade candle waxes and the IGI BOLER, INC. analytical procedure upon request. For the reaons discussed above we do not routinely run G.C. tests for Certificates of Analysis nor commit to G.C. 'envelopes' in product specifications without special arrangements.

2/90

The INTERNATIONAL Group

INTER-COMPANY MEMO

TO: Don Brown
DATE: April 19, 1985
FROM: D. Gill
COPIES TO:
SUBJECT: Test Method: 18D

There are several non critical settings in this method which we from time to time adjust without note. These occur when, for example, the column is clipped due to breakage or non volatile build up and the head pressure is adjusted to compensate. These are acceptable as long as the resolution is not drastically altered. There could also be a better arrangement of equipment available. We use the HP 5880A GC with pressure flow control but any instrument equipped for capillary columns with FID detection would be suitable and a flow programmer would be superior. It must be considered however that if there are major changes in the system the results obtained may not match ours.

DG/rg

International Waxes Limited
50 Salome Drive, Agincourt, Ontario, Canada M1S 2A8 (416) 293-4151 Telex 065 25338

WAX ANALYSIS BY GLC

Test Method: 18D

Method by: D. Gill

Date: April/85

Background: Paraffin waxes, micro waxes and blends thereof consist of several homologeous series in a crystal matrix. This is a method for determining quantitatively the normal hydrocarbon series and several of the non normal series. The modifications over method 18C are necessary for two reasons: 1) To accommodate a new development in capillary liquid phases (ie. the bonded phase), 2) Since we have switched carrier gases from helium to hydrogen.

Method:

1. Start up GLC as per instructions given in "Start Up" below.

2. Make sure that there are no non-volatile components in the sample (this may be accomplished by several methods i.e.: infrared, hot MEK, etc.)

3. Make up solution of 0.0050g sample in 5.0g tetrachloroethylene (o.1% solution).

4. Inject 0.1 ul of sample via on column technique.

5. Analyze the chormatogramme as per instructions in "Analysis" section below.

Start Up:

1. Make sure all gases are turned on at the tanks. Helium and air are located with the other cylinders in the instrument room. Hydrogen is located outside between office and warehouse outer walls and the key hangs on inside of GLC control panel door.

2. Make sure hydrogen supplied are turned OFF at control panel. (Both flow & detector)

3. Turn on all gases at valves behind GLC.

4. Make sure all settings are correct (see "GLC Conditions" below).

5. Turn on injector 2 and detector 2 temperatures.

6. Once detector 2 temperature is above 200°C, turn on oven temperature.

.../2

The INTERNATIONAL Group
BAYCHEM INTERNATIONAL, INC., Houston, Texas • BOLER PETROLEUM COMPANY, Wayne, Pennsylvania • MALCOLM NICOL & CO. INC., Lyndhurst, New Jersey

Start Up:

7. Turn on detector air flow at control panel.

7A. Turn on carrier flow and set such that there is approximately 60 ml/min through the split vent and approximately 10 ml/min through the vent. The column head pressure should have been set to produce a convenient column flow (~1 to 5 ml/min) as determined by Van Demmeter plots.

8. Place ignitor switch (on control panel) into the auto position.

9. Start a plot of the detector signal.

10. Turn on detector hydrogen flow at control panel.

11. Detector should light, indicated by a jump in the plotted signal, within ten - twenty seconds.

12. If detector does not light, consult the manuals.

13. Once detector signal has stabilized, zero the signal, a zero > 20 is common.

14. Stop the plot.

15. Once all conditions have stabilized, press Start Run and allow the system to have a complete blank run.

16. After the blank run is completed, check the chart for peaks and/or base line fluctuations. If none are found, the instrument is ready for injection.

17. If peaks are noted, do another blank run.

18. If baseline fluctuation is noted, run a column compensation.

*GLC Conditions:

1. Column - 30 metre capillary column

2. Liquid phase - SE30 or OV 101 or DB-1 (preferred)

3. Injector temperature 120°C

4. Detector temperature 365°C

5. Oven temperature initial value 110°C

6. Oven temperature initial time 1.0 min.

7. Level #1 Programme:
Oven temperature programme rate 30°C/min
Oven temperature final value 170°C
Oven temperature final time 0 min.

8. Level #3 Programme:
Oven temperature programme rate 10°C/min
Oven temperature final value 350°C
Oven temperature final time 24.9 min.

*GLC Conditions:

9. Signal = D

10. Chart Speed = 1.00 cm/min (optional)

11. Attenuation = 2↑5 (optional)

12. All values off

13. Threshold 0

14. Peak Width 0.02

15. Run Table:
    1. 1.0 min extended run time on
    2. 3.3 min inj #2 temp off
    3. 45.0 min stop

*Note: These conditions give a 45 min (or less) run. If longer runs are desired, extend oven temp. final time.

16. Detector: Flame ionization detector
Hydrogen flow~32 ml/min
Air flow~300 ml/min
Helium make up gas~30 ml/min (25 psi)

17. Column Flow - hydrogen 1-4 ml/min

Note: Pressures quoted in 16 & 17 above read from gauges found on the control panel.

Analysis:

1. Set report to area % mode.

2. Report Table

A. At 0.0 min. select 1. reject 1 x 10" and 2. base line mode #4

B. At some point before, but close to, the start of the 1st peak of interest, select, 1) reject -5 and 2) baseline point.

C. At some point before, but close to the start of the last peak, select baseline point.

3. List report, Under peak type, you should note the letter VV for all but the first peak. The baseline values under "baseline" should be slowly increasing or decreasing or all equal. If these situations are not noted, there has been an error in 1) setting up the report table, 2) the run.

4. Once the report has been obtained, identify the normal peaks by carbon number (see "identification" below).

5. All non normal peaks preceeding each normal peak are assigned the carbon number of that normal.

6. Fill in GLC report form.

.../4

Analysis:

7. Use the Graph programme with the Perkin Elmer 3500 data station to produce a normalized plot of Area % vs. Carbon number.

Indentification:

With any change of column or the change of Any of the GLC conditions, the first run made must be that of a sample (or solvent) spiked with C-28 (or any other analytical standard of normal hydrocarbon above 17 and below 50) to establish a retention time which can be used to identify this same peak in subsequent runs. A sample analysis identification and report are attached.

Note that the following must be included in the report:

1. Total area counts
2. Base line mode used and position of base line points
3. Sum of all area %'s for normals
4. Sum of all area %'s for isomers
5. Any variations made to this method

APPENDIX C

ALLIED-SIGNAL INCORPORATED

APPENDIX C
ALLIED-SIGNAL INCORPORATED

A-C®POLYETHYLENES

TECHNICAL DATA

A-C® 400A Copolymer

Specification No.: 604001227 Supersedes: 4/1/82 Date: 2 1 86

Material Specifications

Item	Allied Test Method	Specifications
Color	W-303-TW	60 Klett Max
Hardness @ 25°C (77°F)	W-301-TW	7-11 dmm
Particle Size through 12 mesh	W-309-TW	98% Min
Vinyl Acetate Content	W-318-TW	12-16%

Average Analysis of Standard Production

Drop Point, Mettler	95°C (203°F)
Density	0.92 g/cc
Viscosity @ 140°C (284°F) Brookfield	550 cps
Bulk Density	513 kg/m^3 (32 lb/ft^3)

Product Form and Packaging

Product is supplied as a white powder, essentially free of foreign material. It is packaged in 25 kg four-ply Kraft bags and shipped on pallets, 40 bags to a pallet, net weight 1,000 kgs, and stretch-wrapped. Pallet loads are approximately 1.29m long, 1.09m wide, and 1.47m high (51 inches x 43 inches x 58 inches).

Safety Precautions

A-C® polyethylenes and copolymers are regarded as non-hazardous when exposure is controlled and good manufacturing practices are employed. Material Safety Data Sheets and safe handling information are available on request.

Additional Information

To place an order, obtain prices, samples and technical information in the continental United States, call toll-free: 1-800-222-0094 (in New Jersey 1-800-222-0095). Or Write: Accounts Manager –
A-C® Polyethylene, Allied-Signal Inc., P.O. Box 2332R, Morristown, NJ 07960

Allied Signal A-C®POLYETHYLENES

TYPICAL PROPERTIES OF A-C® POLYETHYLENES & COPOLYMERS

	Mettler Drop Point (ASTM D-3104)		Hardness dmm (ASTM D-5)	Density g/cc (ASTM D-1505)
Homopolymers	°C	°F		
A-C 6, A-C 6A	106	223	4.0	0.92
7, 7A	107	225	2.5	0.92
8, 8A	116	241	1.0	0.93
9, 9A	117	243	0.5	0.94
617, 617A	102	216	7.0	0.91
712	108	226	3.5	0.92
715	109	228	2.5	0.92
725	108	226	3.5	0.92
735	110	230	2.5	0.92
1702	92	198	90.0*	0.88
Oxidized Homopolymers				
A-C 629, A-C 629A	102	216	5.5	0.93
655	107	225	2.5	0.93
656	100	212	9.0	0.92
680	110	230	1.5	0.94
High Density Oxidized Homopolymers				
A-C 316, A-C 316A	140	284	<0.5	0.98
325	137	279	<0.5	0.99
330	137	279	<0.5	0.99
392	138	280	<0.5	0.99
395	137	279	<0.5	1.00
Copolymers				
Ethylene-Acrylic Acid				
A-C 540, A-C 540A	108	226	2.0	0.93
580	102	216	4.0	0.93
5120	92	198	11.5	0.93
Ethylene-Vinyl Acetate				
A-C 400, A-C 400A	95	203	9.5	0.92
405(S)	95	203	7	0.92
405(M)	99	210	5	0.92
405(T)	103	217	4	0.92
430	60	140	80.0*	0.93
Micronized Polyethylene Waxes				
POLYMIST® A-12	136	277	<0.5	0.99
B-6	126	259	<0.5	0.96
B-12	126	259	<0.5	0.96

*ASTM D-1321

	Viscosity-cps @ 140°C (Brookfield)	Acid Number mg KOH/g	Physical Form	Packaging
Homopolymers				
A-C 6, A-C 6A	350	Nil	Prills, Powder	25 kg Bag
7, 7A	350	Nil	Prills, Powder	25 kg Bag
8, 8A	400	Nil	Prills, Powder	25 kg Bag
9, 9A	450	Nil	Prills, Powder	25 kg Bag
617, 617A	180	Nil	Prills, Powder	25 kg Bag
712	1600	Nil	Diced	25 kg Bag
715	4000	Nil	Diced	25 kg Bag
725	1400	Nil	Diced	25 kg Bag
735	6000	Nil	Diced	25 kg Bag
1702	40	Nil	Grease-like	50 kg Drum
Oxidized Homopolymers				
A-C 629, A-C 629A	200	16	Prills, Powder	25 kg Bag
655	210	16	Prills	25 kg Bag
656	185	15	Prills	25 kg Bag
680	250	16	Prills	25 kg Bag
High Density Oxidized Homopolymers				
A-C 316, A-C 316A	8500 (@ 150°C)	16	Granule, Powder	25 kg Bag
325	4400 (@ 150°C)	25	Granule	25 kg Bag
330	3600 (@ 150°C)	30	Granule	25 kg Bag
392	4500 (@ 150°C)	30	Granule	25 kg Bag
395	2500 (@ 150°C)	41	Granule	25 kg Bag
Copolymers				
Ethylene-Acrylic Acid				
A-C 540, A-C 540A	500	40	Prills, Powder	25 kg Bag
580	650	75	Prills	25 kg Bag
5120	650	120	Prills	50 kg Drum
Ethylene-Vinyl Acetate		% Vinyl Acetate		
A-C 400, A-C 400A	610	13	Prills, Powder	25 kg Bag
405(S)	600	11	Prills	25 kg Bag
405(M)	600	8	Prills	25 kg Bag
405(T)	600	6	Prills	25 kg Bag
430	600	26	Grease-like	50 kg Drum
Micronized Polyethylene Waxes	Average Particle Size (Microns)	Acid Number mg KOH/g		
POLYMIST® A-12	12	30	Micronized Powder	50 kg Drum
B-6	6	Nil	Micronized Powder	50 kg Drum
B-12	12	Nil	Micronized Powder	50 kg Drum

APPENDIX D

ARCO CHEMICAL COMPANY

APPENDIX D
ARCO CHEMICAL COMPANY

ARCONATE® Propylene Carbonate

Product Information

Arconate Propylene Carbonate is an easily handled, high boiling, oxygenated solvent exempt from Rule 66. It has a low order of toxicity and broad solvent powers for organic and inorganic materials. It is a cyclic ester and undergoes most reactions typical for this class of products. For example, Arconate PC reacts with amines to form carbamates, undergoes hydroxy alkylation reactions (often succeeding where propylene oxide reaction is difficult), transesterification, and the formation of polycarbonates. Hydrolysis of Arconate PC yields propylene glycol.

Arconate® HP

Propylene Carbonate

Product Data

PROPERTY	TYPICAL VALUES	TEST METHOD
Suspended Matter	Substantially Free	ASTM D-2849
Residue on Ignition, wt. %, max	0.01	USP XXI
Color, Pt-Co, max.	40	ASTM D-1209
Odor	Mild	ACC 12610
pH, 10% aqueous solution	6.5-7.5	ASTM D-1287
Specific Gravity @ 20/20°C	1.203-1.210	ASTM D-891
Assay, wt. % PC, min.	99.8	ACC 6106

Typical Physical Properties for Both Arconate HP and 1000

Boiling Point, °C (°F)	242 (468)
Dielectric Constant, esu @ 25°	64
Flash Point, Tag Open Cup, °C (°F)	132 (270)
Freezing Point, °C (°F)	−50 (−48)
Refractive Index, 25°C	1.419
Density, 20°C, gm/cc (lbs/gal)	1.206 (10.1)
Vapor Pressure, 20°C, mmHg	0.02
Viscosity, CS, 25°C	4

Arconate® 1000

Propylene Carbonate

Product Data

PROPERTY	TYPICAL VALUES	TEST METHOD
Suspended Matter	Substantially Free	ASTM D-2849
Residue on Ignition, wt. %, max	0.01	USP XXI
Color, Pt-Co, max.	300-500	ASTM D-1209
Odor	Mild, not objectionable	ACC 12610
pH, 10% aqueous solution	4.5-6.5	ASTM D-1287
Specific Gravity @ 20/20°C	1.203-1.210	ASTM D-891
Assay, wt. % PC, min.	99.0	ACC 6106

[redacted]

ARCO Chemical Company

Printed in U.S.A. ACC OP20A 488 3M

Valid for
5/18/94
Only

ARCO Chemical Company
SALES SPECIFICATIONS
UN-CONTROLLED DOCUMENT

Page: 1

Resource Code: PC1000
Material Desc: PROP. CARBONATE 1000

Customer Code:
Class:
Revised Date: 5/03/94

Revision No:001 - SPECIFICATION UPDATE

Approvals:	D.R. MATHERA	5/03/94	J.F. SULLIVAN	5/03/94
	R.A. HECKMAN	5/03/94	T.E. HIETT	5/03/94

Using Location No. 1:

No. 2:

Material Specifications

Requirement	Unit	Min/Max		Limits	Test	SQC	COA
Assay as PC	wt. %	99			HOC-0536		
Color, APHA (by Hunter Colorimeter)			500		HOC-0920		
pH, 10% Aqueous Solution Range		4.0	8.5		HOC-0103		
*Residue on Ignition	wt. %		0.01		HOC-0140		
*Specific Gravity @ 20/20	degree C	1.203	1.210		HOC-0132		
Suspended Matter				Free Substantially free	HOC-0171		

*= These properties are analyzed on a quarterly basis

**** END OF REPORT ****

APPENDIX E

EXXON COMPANY USA

APPENDIX E
EXXON COMPANY USA

TYPICAL INSPECTIONS

The values shown here are representative of current production. Some are controlled by manufacturing specifications, while others are not. All may vary within modest ranges.

PRODUCT	Viscosity				Color ASTM	Gravity °API	Density at 15 °C (59 °F)	Pounds per gallon at 15.6 °C (60 °F)	Aniline Point		Pour Point		Flash Point	
	cSt at		SSU at											
	40 C	100 C	100 F	210 °F					C	°F	C	°F	°C	°F
AROMATIC														
TELURA 126*	22.4	3.5	119	38.0	L1.5	15.8	0.960	8.00	32	89	-37	-35	168	335
TELURA 171*	129.7	8.5	703	55.5	L3.5	15.8	0.960	8.00	51	123	-21	-5	177	350
NAPHTHENIC														
TELURA 315	15.6	3.1	85	36.9	L0.5	26.9	0.893	7.44	76	168	-40	-40	157	315
TELURA 323	20.8	3.8	110	38.9	L1.0	26.3	0.896	7.47	78	172	-35	-33	166	330
TELURA 330	29.3	4.7	160	41.9	L1.0	25.5	0.901	7.51	81	177	-34	-30	168	335
TELURA 343	45.7	5.8	238	45.9	L1.0	24.7	0.905	7.54	83	181	-21	-5	182	360
EXTRACTED NAPHTHENIC														
TELURA 401	2.8	1.1	36	—	L0.5	36.3	0.843	7.02	71	160	-73	-100	102	215
TELURA 407[1]	8.7	2.3	56	33.8	L0.5	30.5	0.873	7.27	78	172	-54	-65	149	300
TELURA 415[2]	14.1	3.2	79	36.7	L0.5	30.2	0.875	7.29	86	186	-39	-38	160	320
TELURA 417[2]	18.5	3.6	99	38.5	L1.0	29.3	0.880	7.33	88	191	-33	-27	171	340
PARAFFINIC														
TELURA 515*	14.5	3.2	80	37.0	L2.5	28.9	0.882	7.35	83	182	-7	20	149	300
TELURA 521[2]	21.0	4.0	110	39.7	0.5	30.2	0.875	7.29	96	204	-15	5	179	355
EXTRACTED PARAFFINIC														
TELURA 607[2]	7.0	2.1	50	33.4	L0.5	36.2	0.843	7.03	91	196	-11	12	154	310
TELURA 612[2]	13.0	3.6	74	38.3	L0.5	35.1	0.849	7.07	99	211	-18	0	188	370
TELURA 613[2]	13.3	3.1	75	36.8	L0.5	34.0	0.855	7.12	96	205	-21	-5	182	360
TELURA 619[2]	20.0	4.0	105	39.7	L0.5	32.5	0.862	7.18	99	210	-18	0	193	380
TELURA 662	64.1	8.4	332	54.3	L1.5	29.4	0.879	7.32	112	233	-9	15	227	440
TELURA 668	86.5	10.3	450	61.3	1.0	29.1	0.881	7.34	116	240	-9	15	232	450
TELURA 671	111.7	12.0	583	67.7	L2.0	29.2	0.880	7.33	117	243	-9	15	249	480
SPECIAL GRADE														
TELURA 797	—	210.8	—	1038	8	11.5	0.989	8.24	—	—	13	55	213	415

1 Contains Oxidation Inhibitor
2 Meets 21CFR 178.3620(c)
* Possible carcinogen under current OSHA criteria

Neut. No. mg KOH/g	Sulfur, Mass %	Volatility, 3 hours at 163 C (325 F), Mass % Loss	Clay/Silica Gel Analysis, Mass %				Carbon Type Analysis			Refractive Index at 20 C	Viscosity-Gravity Constant	Approximate GC Distillation Range		
			Aromatics	Saturates	Polars	Asphaltenes	C_N	C_P	C_A			IBP F	50% F	FBP F
0.14	1.45	2.6	68.5	29.2	2.3	0	26	39	35	1.537	0.934	484	672	862
0.05	1.00	0.7	56.2	40.3	3.5	0	35	34	31	1.536	0.916	507	805	992
0.01	0.03	4.2	34.2	65.5	0.3	0	36	51	13	1.492	0.857	469	681	900
0.01	0.07	4.1	35.3	64.0	0.7	0	35	52	13	1.493	0.825	472	707	953
0.03	0.04	1.6	35.8	62.9	1.3	0	33	53	14	1.497	0.855	478	735	976
0.09	0.04	1.1	36.0	63.0	1.0	0	33	53	14	1.499	0.856	486	765	984
0.01	0.01	29.3	19.5	80.4	0.1	0	38	56	6	1.461	0.836	344	484	612
0.01	0.14	5.2	23.6	76.2	0.2	0	39	53	8	1.480	0.844	461	626	805
0.02	0.29	3.1	21.1	78.8	0.1	0	44	52	4	1.480	0.837	474	683	890
0.01	0.19	2.9	23.0	76.9	0.1	0	38	56	6	1.482	0.838	475	704	957
0.18	0.53	4.2	29.0	70.0	1.0	0	32	57	11	1.486	0.845	452	706	988
0.01	0.16	1.1	18.9	80.8	0.3	0	35	60	5	1.479	0.830	530	740	988
0.02	0.16	4.9	17.6	82.3	0.1	0	29	64	7	1.469	0.815	473	639	841
0.01	0.13	1.3	15.0	84.9	0.1	0	27	70	3	1.467	0.808	523	719	815
0.01	0.17	1.5	13.0	86.8	0.2	0	28	68	4	1.471	0.814	489	715	893
0.03	0.23	1.4	17.9	81.8	0.3	0	28	67	5	1.475	0.816	522	782	933
0.01	0.46	0.3	20.7	78.5	0.8	0	28	67	5	1.483	0.816	610	892	1133
0.01	0.45	0.3	20.2	79.3	0.5	0	29	67	4	1.484	0.807	644	930	1147
0.01	0.44	0.13	19.1	80.0	0.9	0	29	67	4	1.485	0.807	617	953	1133
—	3.2	0.3	31.8	28.7	21.9	17.6	—	—	—	—	0.891	—	—	—

APPENDIX F

INDUSTRIAL RAW MATERIALS CORPORATION

APPENDIX F
INDUSTRIAL RAW MATERIALS CORPORATION

INDUSTRIAL RAW MATERIALS CORP.

575 MADISON AVENUE · NEW YORK, N.Y. 10022 · TELEPHONE (212) 688-8080

CABLE: INDRAW NEW YORK
RCA TELEX 232636
WESTERN UNION: 12—7004
FAX 212-759-3696

TYPICAL SPECIFICATIONS

INDRAMIC 800

DESENSITIZING WAX

	MIL W -20553-D REQUIREMENT		INDRAMIC 800 TYPICALS
	MINIMUM	MAXIMUM	
Melting Point °F ASTM D-127	175	200	181-192
Viscosity @ 210°F cst. ASTM D-445	15	21	15-18
Penetration ASTM D-1321 @ 77°F	6		12-17
@ 110°F		35	24-30
Flash Point °F ASTM D-92	500		500
% Oil Content ASTM D-721		2.5	2.0
% Organic Materials	Nil		-
% Alkalinity	None		-
% Acidity	None		-
% Exudation 160°F		3.0	1.0

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WESTERN UNION: 12—7004
FAX 212-759-3696

TYPICAL SPECIFICATIONS

INDRAMIC 170-C

DESENSITIZING WAX

	MIL W -20553-D REQUIREMENT		INDRAMIC 170-C TYPICALS
	MINIMUM	MAXIMUM	
Melting Point °F ASTM D-127	175	200	182-186
Viscosity @ 210°F cst ASTM D-445	15	21	15-18
Penetration ASTM D-1321 @ 77°F	6		12-16
@ 110°F		35	24-30
Flash Point °F ASTM D-92	500		500
% Oil Content ASTM D-721		2.5	1.0
% Organic Materials	Nil		-
% Alkalinity	None		-
% Acidity	None		-
% Exudation 160°F		3.0	1.2

APPENDIX G

MONSANTO COMPANY

APPENDIX G
MONSANTO COMPANY

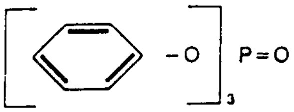
Publication No. 1544

PLASTICIZERS

Triphenyl Phosphate

Flame-retarding Plasticizer for Cellulosic Materials

Triphenyl Phosphate



Triphenyl phosphate – a solid – is the most commonly used flame retardant* for cellulose acetate. It is compatible with many vinyl resins, cellulosics and synthetic rubber. In vinyl compounds, however, it should be used in conjunction with a liquid plasticizer to prevent crystallizing and blooming.

In cellulose acetate films, triphenyl phosphate imparts flame resistance, good clarity, excellent water resistance, good flexibility and toughness with no tendency toward tackiness.

Triphenyl phosphate improves tensile strength in nitrocellulose films, and it imparts other favorable properties similar to its effect in cellulose acetate.

Synthetic rubbers benefit from triphenyl phosphate's fair softening action and a resistance to extraction by gasoline and mineral oils.

In some engineering thermoplastics, triphenyl phosphate imparts excellent fire retardance and processing with minimal loss of strength.

Toxicity and Handling

Triphenyl phosphate can be used in certain indirect food contact applications. Regulations appear in Title 21, Code of Federal Regulations, Sections 175.105 and 177.2420 (as solvent). Based upon toxicity studies, triphenyl phosphate has a low order of toxicity and does not require special handling. Handle in accordance with good industrial hygiene and safety practices. These practices include avoiding unnecessary exposure and removal of the material from eyes, skin and clothing. Complete toxicity and handling information can be found on the Material Safety Data Sheet which is available upon request.

Table A. Properties

Molecular Weight	326
Phosphorus, %	9.5 (Calc)
• Acidity (meq/100 gm. max)	0.10
• Appearance	White flakes
• Color (APHA) [max.]	20 (molten)
• Odor (max.)	Very faint, aromatic
Refractive Index (@ 60°C)	1.550
Specific Gravity (60°/20°C)	1.268
Density (@ 60°C) ca. lbs./gal.	10.5
Crystallizing Point (°C)	49
Boiling Point @ 10mm Hg, °C	238
Vapor Pressure (mm Hg)	
@ 150°C	>0.1
@ 200°C	1.3
@ 250°C	18.2
Viscosity (Centistokes)	
@ 55°C	7.8
@ 98.9°C	2.9
Flash Point (C.O.C.) [°F.]	437
Solubility In Water @ 34°C, %	0.002
CAS Number	115-86-6

• Specification

®Registered Trademark of Monsanto Company

*"Flame retardant," "fire retardant" and similar phrases used to describe this product merely denote a relative quality. These terms do not mean that flame-retardant additives will not burn or that they will totally eliminate burning. Rather, Monsanto's flame-retardant additives are useful in helping customers formulate or construct finished products meeting fire codes and fire safety regulations.

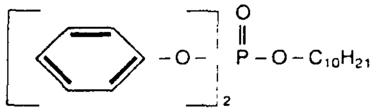
POLYMER MODIFIERS
Monsanto

Publication No 1541A

SANTICIZER® 148

Flame-retardant, Low-temperature Plasticizer With Low Volatility

Isodecyl Diphenyl Phosphate



Santicizer® 148 is an efficient flame retardant*, excellent for many commercial resins, particularly polyvinyl chloride and its copolymers, polyvinyl acetate and acrylics. It is high solvating and provides good low-temperature flexibility, and it is miscible with most common solvents.

Santicizer 148 imparts flame retardance, low-temperature flexibility and low volatility in polyvinyl chloride. It can replace DOP part-for-part to the level needed for fire retardancy while maintaining the flexibility and the softening efficiency of that phthalate. Its use in the compound imparts low smoke-generation performance that is far superior to triaryl phosphates or antimony oxide. It also offers superior fusion properties and solvating action and imparts resistance to abrasion, oil and grease. Used as a 10%-15% replacement for phthalates, it has excellent weather and light stability. Hand and drape of the finished film or coated fabric containing Santicizer 148 are outstanding.

In vinyl plastisols, Santicizer 148 exhibits fast fusion, low initial viscosity and viscosity stability. Cell structure of vinyl foams is excellent. Clear formulations show a sparkling clarity with Santicizer 148. The cured compound possesses good low-temperature flexibility and flame retardance.

Santicizer 148 offers PVC adhesives – such as laminating adhesives – fast fusion, good viscosity and flame retardance. When laminating PVC film to cloth, the use of a fire-retardant adhesive dramatically reduces the flammability of the laminate.

By the addition of silica aerogel and a non-ionic detergent, a shear-sensitive gel of Santicizer 148 can be applied to expanded-glass air filters. Such treated filters are flame retardant and efficient dust collectors.

Santicizer 148 is an efficient low volatility solvator for ethyl cellulose, nitrocellulose, SBR and nitrile (Buna N) rubbers.

Flame-retardance Performance

Vinyl compositions properly formulated with Santicizer® 148 show excellent performance in both flame-spread and smoke generation characteristics.

As with phthalate and triaryl phosphate plasticizers, the inclusion of antimony trioxide

Table A. Properties

Molecular Weight	390
Phosphorus, %	7.9 (Calc)
• Acidity (meq. 100 gm. max)	0.20
• Appearance	Clear, oily liquid
• Color (APHA) [max.]	100
• Moisture (KF in Methanol) %, max.	0.10
• Odor	Essentially odorless
• Refractive Index (@ 25°C)	1.501 — 1.507
• Specific Gravity (25°/25°C)	1.061 — 1.071
Density (@ 25°C) ca. lbs./gal.	8.94
Crystallizing Point (°C)	< −35
Pour Point (°C)	< −50
Boiling Point @ 10mm Hg, °C	245 (decomposes)
Vapor Pressure (mm Hg)	
@ 150°C	<0.1
@ 200°C	0.5
Viscosity (Centistokes)	
@ 0°C	95
@ 25°C	22.5
@ 98.9°C	3.0
Flash Point (C.O.C.) [°F.]	465
Fire Point (C.O.C.) [°F.]	500
Thermal Expansion Coefficient @ 10° – 40°C (cc/cc/°C)	0.00071
Solubility In Water @ 25°C, %	<0.0008
CAS Number	29761-21-5

• Specification

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*"Flame retardant," "fire retardant" and similar phrases used to describe this product merely denote a relative quality. These terms do not mean that flame-retardant additives will not burn or that they will totally eliminate burning. Rather, Monsanto's flame-retardant additives are useful in helping customers formulate or construct finished products meeting fire codes and fire safety regulations.

APPENDIX H

PETROLITE CORPORATION

APPENDIX H
PETROLITE CORPORATION

TECHNICAL DATA

TECHNICAL RELEASE BP137

POLYWAX® 600 Polyethylene

Specification Midpoint

Property	Test	Units	POLYWAX 600 Polyethylene
Viscosity @ 300°F (149°C)	ASTM D-88	SSU	64
Penetration @ 77°F (25°C)	ASTM D-1321	0.1 mm	3
@ 140°F (60°C)			28
Melt Point	ASTM D-127	°F (°C)	202 (94)
Color	ASTM D-156		13

4/90

PETROLITE SPECIALTY POLYMERS GROUP
6910 EAST 14TH STREET • TULSA, OK 74112 • (918) 836-1601 • TWX 910-845-2193 • FAX 918-834-9718

P-1227 (R4/90)

TECHNICAL DATA

TECHNICAL RELEASE BP100

POLYWAX® Polyethylenes

Typical Properties

Property	Test	Units	POLYWAX 500 PE	POLYWAX 655 PE	POLYWAX 850 PE	POLYWAX 1000 PE	POLYWAX 2000 PE	POLYWAX 3000 PE*
Melting Point**	ASTM D 127	°F (°C)	190(88)	211(99)	225(107)	235(113)	258.5(126)	265(129)
Ring and Ball	ASTM D 36 Mod.	°F (°C)	190(88)	211(99)	225(107)	235(113)	258.5(126)	265(129)
Molecular Weight	Vapor Pressure Osmometry	–	500	655	850	1000	2000	3000
Polydispersity	Gel Permeation Chromatography	–	1.08	1.08	1.08	1.08	1.10	1.10
Melt Index	ASTM D 1238 FR-A	grams/ 10 min	> 5000	> 5000	> 5000	> 5000	> 5000	> 5000
Viscosity								
@210°F (99°C)	ASTM D 88	SUS**	54					
@300°F (149°C)	ASTM D 88	SUS**		47	62	80	290	775
@300°F (149°C)	ASTM D 3236	cP		5	8	12	49	130
Penetration								
@77°F (25°C)**	ASTM D-1321	0.1mm	6.5	2.0	2.0	1.0	0.5	0.5
@140°F (60°C)**			52	16	7.5	4.5	1.5	1.0
Density								
@ 77°F (25°C)	ASTM D 792 Mod.	g/cc	0.93	0.94	0.96	0.96	0.97	0.98
@ 300°F (149°C)	ASTM D 1298	g/cc	0.74	0.75	0.76	0.76	0.77	0.78

* Target values
** Specification midpoint

POLYWAX polyethylenes are crystalline aliphatic hydrocarbons having a narrow molecular weight distributions. There are six POLYWAX polyethylenes with average molecular weights ranging from 500 to 3000.

POLYWAX polyethylenes are homopolymers of ethylene produced by the Petrolite Specialty Polymers Group. Chemically, POLYWAX polyethylenes are fully saturated normal hydrocarbons and are high molecular weight paraffin analogs.

R1/91

PETROLITE

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P 1227 R6/91

APPENDIX I

SHELL CHEMICAL CO.

APPENDIX I
SHELL CHEMICAL CO.

			KRATON® G Rubber							KRATON® FG Rubber		Table I
Kraton G-1650 (SEBS)[6] Linear	Kraton G-1652 (SEBS)[6] Linear		Kraton® G-1654X (SEBS)[6] Linear	Kraton G-1657 (SEBS)[6] Linear	Kraton® G-1701X (SEP)[6] Diblock	Kraton® G-1702X (SEP)[6] Diblock	Kraton® G-1726X (SEBS)[6] Linear	Kraton® G-1750X (EP)$_n$[5] Multi-arm	Kraton® G-1765X (EP)$_n$[6] Multi-arm	Kraton® FG-1901X (SEBS)[6] Linear	Kraton® FG-1921X (SEBS)[6] Linear	Property
5000[2]	4500[2]		3500	3400[2]	300[2]	300[2]	350[2]	<50	<50	5000	5000	Tensile Strength, psi[1]
800	700		900	350	—	—	—	—	—	—	—	300% Modulus, psi[1]
500	500		700	750	<100	<100	200	100	120	500	500	Elongation, %[1]
—	—		—	—	—	—	—	—	—	—	—	Set at Break, %
75	75		75	65	72	75	60	18	23	75	75	Hardness, Shore A
0.91	0.91		0.92	0.90	0.92	0.91	0.91	0.86	0.86	0.91	0.91	Specific Gravity
8000[4]	1350[4]		370[5]	4200[4]	>50000[4]	>50000[4]	200[4]	8720	12600	1250[5]	—	Brookfield Viscosity (Toluene Solution) cps at 77 °F
—	10		-	8	—	—	65	7.5	4.2	22	—	Melt Viscosity, Melt Index, Condition G, gms/10 min
0	0		0	0	0	0	0	0	12	0	0	Plasticizer Oil Content, %w
29/71	29/71		31/69	13/87	37/63	28/72	30/70	—	—	—	—	Styrene/Rubber Ratio
Powder	Powder		Powder	Pellet	Powder	Powder	Pellet	Bale	Bale	Pellet	Pellet	Physical Form[3]
FDA[7]	FDA[7]		—	35% Diblock	—	—	FDA[7] 70% Diblock	—	—	FDA[7] 1% bound functionality (as succinic anhydride)	FDA[7] 1% bound functionality (as succinic anhydride)	Comments

KRATON® D and KRATON® G Rubber

For use as an additive or a major formulating ingredient

Summary of typical properties at 74 °F
These are typical values and should not be used to set specifications.

Table I KRATON® D Rubber

Property	Kraton D-1101 (SBS)^8 Linear	Kraton D-1102 (SBS)^8 Linear	Kraton D-1107 (SIS)^8 Linear	Kraton D-1111 (SIS)^8 Linear	Kraton D-1112 (SIS)^8 Linear	Kraton* D-1113X (SIS)^8 Linear	Kraton* D-1114X (SIS)^8 Linear	Kraton D-1116 (SB)$_n^8$ Branched	Kraton D-1117 (SIS)^8 Linear	Kraton* D-1118X (SB)^8 Diblock	Kraton* D-1122X (SB)$_n^8$ Branched
Tensile Strength, psi^1	**4600**^{2}	**4600**^{2}	**3100**^{2}	**2900**^{2}	**1500**^{2}	600	—	4600^{10}	1200^2	250^2	3200
300% Modulus, psi^1	400	400	100	200	70	50	—	350	60	175	650
Elongation, %^{1}	**880**	**880**	1300	1200	1400	1500	—	900	1300	600	750
Set at Break, %	10	10	10	10	20	20	—	10	15	40	20
Hardness, Shore A	**71**	**71**	**37**	**52**	**34**	—	—	65	32	61	78
Specific Gravity	0.94	0.94	0.92	0.93	0.92	0.92	0.92	0.94	0.92	0.94	0.95
Brookfield Viscosity (Toluene Solution), cps at 77 °F	**4000**^{4}	**1200**^{4}	**1450**^{4}	**1200**^{4}	**900**^{4}	600	700	9000^4	500^4	850^4	730
Melt Viscosity, Melt Index, Condition G, gms/10 min.	<1	6	11	3	23	—	—	<1	106	10	3
Plasticizer Oil Content, %w	**0**	**0**	**0**	**0**	**0**	0	0	0	0	0	0
Styrene/Rubber Ratio	31/69	28/72	14/86	22/78	14/86	16/84	19/81	21/79	17/83	30/70	37/63
Physical Form^9	**Porous Pellet, Powder**	**Porous Pellet, Powder**	**Pellet**	**Porous Pellet**	**Pellet**	Pellet	Pellet	Porous Pellet, Powder	Pellet	Porous Pellet, Powder	Porous Pellet
Comments	FDA^7	FDA^7	FDA^7	FDA^7	FDA^7 40% Diblock	FDA^7 55% Diblock	FDA^7 0% Diblock	—	FDA^7 40% Diblock	FDA^7 80% Diblock	FDA^7

1. ASTM method D-412-tensile tester jaw separation speed 10 in./min.
2. Typical properties determined on film cast from a toluene solution.
3. Typical values on polymer compression molded at 300 °F.
4. Neat polymer concentration, 25%w.
5. Neat polymer concentration, 15%w.
6. Plasticized polymer concentration, 25%w.
7. FDA Regulated Applications–Kraton D and Kraton G 1000 series products find use under certain FDA regulations as articles or as ingredients in articles intendec to another. For specific clearances, letters of certification will be provided upon request.
8. (SBS) styrene-butadiene-styrene block copolymer. (SIS) styrene-isoprene-styrene block copolymer. (SEBS) styrene-ethylene-butylene-styrene block copolymer (SI)$_n$ styrene-isoprene multi-arm (branched) copolymer. (EP)$_n$ ethylene-propylene multi-arm (branched) polymer
9. Precautions to be taken in handling and storing. Kraton Thermoplastic Rubber can accumulate electrostatic charges when rubbed, chafed, or abraded Equ Compounding of Kraton Thermoplastic Rubber in high shear equipment can cause the temperature to rise. DO NOT ALLOW THE TEMPERATURE TO EXCEE Material Safety Data Sheet of a specific Kraton product for further safety information.
10. Results measured on oil extended films cast from toluene and then extrapolated to zero oil content.
11. Neat polymer concentration, 10%w.

* "X" denotes developmental product.

APPENDIX J

WITCO CHEMICAL CO.

APPENDIX J
WITCO CHEMICAL CO.

Composition and physical properties

Primary amides.

Humko Chemical's Kemamide primary amides are based on fatty saturated and unsaturated straight-chain, monobasic acids derived from naturally occurring feedstocks. Predominant chain lengths range from eighteen to twenty-two carbon atoms. The Kemamide primary amides are waxy solids with melting points in the range 68-108° C.

Composition.

Kemamide S Stearamide *CTFA adopted name:* *Stearamide* Major component: $CH_3(CH_2)_{16}CONH_2$	Saturated fatty primary amide derived from stearic acid. Available in powder and pellet forms.
Kemamide B Arachidamide/Behenamide *CTFA adopted name:* *Behenamide* Major components: $CH_3(CH_2)_{18}CONH_2/CH_3(CH_2)_{20}CONH_2$	Saturated fatty primary amide derived from a mixture of arachidic and behenic acids. Available in powder and pellet forms.
Kemamide U, O Oleamide *CTFA adopted name:* *Oleamide* Major component: $CH_3(CH_2)_7CH{=}CH(CH_2)_7CONH_2$	Unsaturated fatty primary amide derived from oleic acid. Available in powder and pellet form. Kemamide U is a refined grade of oleamide.
Kemamide E Erucamide *CTFA adopted name:* *Erucamide* Major component: $CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CONH_2$	Unsaturated fatty primary amide derived from erucic acid. Available in powder, pellet and mini-pellet forms.

Kemamide slip additives have made polyethylene film easier to produce and handle. Thus, this plastic film has become an unrivaled leader in today's packaging industry.

Physical Properties.

Specifications	Kemamide S	Kemamide B	Kemamide U	Kemamide O	Kemamide E
Acid value, max	4	4	4	5	4
Iodine value	3.0 max	4.0 max	72-90	72-90	70-80
Melting range, °C	98-108	98-108	68-78	66-77	76-86
Color, Gardner (1963), max	4	4	4	7	4
% Moisture, max	0.25	0.25	0.25	0.25	0.25
% Amide by IR, min	95	95	95	95	95
Typical Properties	**Kemamide S**	**Kemamide B**	**Kemamide U**	**Kemamide O**	**Kemamide E**
Molecular weight	278	312	275	275	335
Density @ 130°C (266°F), g/mL	0.809	0.807	0.823	0.822	0.815
Density @ 160°F (71°C), g/mL	0.849	0.843	0.859	0.857	0.851
Viscosity @ 130°C, cP	5.8	6.5	5.5	5.5	6.4
Heat of fusion, kcal/mol	12.2	12.7	6.3	6.3	9.8
Flash point, °C, COC	246	257	245	245	262
Fire point, °C, COC	268	284	264	264	287

Solubility*

Solvent	Kemamide S			Kemamide B			Kemamide U, O			Kemamide E		
Temperature	**40° C**	**50° C**	**60° C**	**40° C**	**50° C**	**60° C**	**10° C**	**20° C**	**30° C**	**15° C**	**25° C**	**35° C**
Chloroform	5	>10	—	6	>10	—	8	22	—	8	25	>30
Isopropyl alcohol	5	10	—	4	9	>10	7	15	>30	3	8	>20
Methyl alcohol	1	3	>10	<1	1	10	3	7	28	1	3	10
Methyl ethyl ketone	2	4	>10	2	5	>10	2	7	>20	2	4	20
Toluene	1	2	6	1	3	10	1	4	25	1	3	14

*Based on g solute/100 g solvent

Secondary amides.

Humko Chemical's secondary amides are products of the reaction of saturated and unsaturated fatty acids with saturated and unsaturated primary amines. A variety of combinations other than those listed opposite can be made to order. The Kemamide secondary amides' principal advantages lie in their lubricity and thermal stability.

Composition.

Kemamide E-180 Stearyl Erucamide *CTFA adopted name.* *Stearyl Erucamide* Major component: R'CONHR O (R'C=erucyl. R=stearyl)	Substituted fatty amide derived from erucic acid and stearyl amine. Available as a white, free-flowing powder.
Kemamide E-221 Erucyl Erucamide Major component: R'CONHR O (R'C=erucyl. R=erucyl)	Substituted fatty amide derived from erucic acid and erucyl amine. Available as a white, free-flowing powder.
Kemamide P-181 Oleyl Palmitamide *CTFA adopted name:* *Oleyl Palmitamide* Major component: R'CONHR O (R'C=palmityl. R=oleyl)	Substituted fatty amide derived from palmitic acid and oleyl amine. Available as a white, free-flowing powder.
Kemamide S-180 Stearyl Stearamide Major component: R'CONHR O (R'C=stearyl. R=stearyl)	Substituted fatty amide derived from stearic acid and stearyl amine. Available as a white, free-flowing powder.
Kemamide S-221 Erucyl Stearamide Major component: R'CONHR O (R'C=stearyl. R=erucyl)	Substituted fatty amide derived from stearic acid and erucyl amine. Available as a white, free-flowing powder.

Kemamide secondary amides are particularly useful in the handling of thermoplastic resins requiring higher processing temperatures.

Physical Properties.

Specifications	Kemamide E-180	Kemamide E-221	Kemamide P-181	Kemamide S-180	Kemamide S-221
Color Gardner (1963), max	4	6	3	4	6
Total amine value, max	3	3	3	3	3
Acid value, max	8	8	8	8	8
Melting range, °C	72-75	55-58	65-70	88-92	76-80
Typical Properties	**Kemamide E-180**	**Kemamide E-221**	**Kemamide P-181**	**Kemamide S-180**	**Kemamide S-221**
Iodine value	44	80	43	1	46
Flash point, °C, CC	258	260	262	246	268
Heat of fusion, cal/g	32.4	29.6	29.6	31.0	31.5
Specific heat, cal/g @ 55°C	0.34	0.40	0.45	0.36	0.48
Specific heat, cal/g @ 164°C	0.42	0.52	0.55	0.48	0.59
Density, g/mL @ 110°C	0.8074	0.8165	0.8076	0.8042	0.7877
Density, g/mL @ 130°C	0.7902	0.7998	0.7935	0.7825	0.7746
Density, g/mL @ 150°C	0.7738	0.7838	0.7798	0.7619	0.7619

Solubility*

Solvent	Kemamide E-180			Kemamide E-221			Kemamide P-181			Kemamide S-180			Kemamide S-221		
Temperature	**30° C**	**40° C**	**50° C**	**20° C**	**30° C**	**40° C**	**30° C**	**40° C**	**50° C**	**50° C**	**60° C**	**70° C**	**40° C**	**50° C**	**60° C**
Chloroform	30	50	<50	35	<50	—	35	<50	—	50	<50	—	45	<50	—
Dichloroethane	1.5	7	50	2	15	<50	1.5	8	<50	3.5	20	<50	3	14	<50
Isopropyl alcohol	2	5	30	1.5	5	50	3	15	<50	3	15	<50	2.5	14	<50
Methyl alcohol	>1	>1	1	>1	>1	1	>1	1	5	>1	1	—	>1	1	—
Methyl ethyl ketone	1	4	25	1	4	30	2	7	50	2.5	15	<50	1.5	7	50
VM & P naphtha	1	3	40	1.5	20	<50	1	15	<50	2	15	<50	1.5	20	<50
Toluene	5	30	<50	15	<50	—	8	50	<50	10	50	<50	20	<50	—

*Based on g solute/100 g solvent

APPENDIX K

ZEON CHEMICALS, INCORPORATED

APPENDIX K
ZEON CHEMICALS, INCORPORATED

Nipol®
NITRILES

NIPOL 1312 LIQUID RUBBER

PRODUCT SPECIFICATION
(Revised 7/17/90)

SPECIFICATION FOR NIPOL 1312

Nipol 1312 is a copolymer of butadiene and acrylonitrile of medium-high oil resistance in liquid form. Sufficient antioxidant is added during manufacture for normal aging conditions. The ingredients comprising Nipol 1312 are acceptable under FDA regulations 175.105 and 177.2600.

SPECIFICATION LIMITS

Nipol 1312 is a viscous liquid and is amber-to-light brown in color. It shall be free from foreign material considered objectionable for normal applications.

CHEMICAL PROPERTIES

Analysis	Specification	Procedure #*
Heat Loss (%, Max.)	0.5	362 Hf
Ash (%, Max.)	0.5	873 Ba
Brookfield Viscosity cps @ Number 4 Spindle, 50°C	20,000-30,000	170 A
Bound Acrylonitrile (%)	27.0-30.0	325 Ea

* Procedures available upon request.

Note: Refer to MSDS #3 for proper handling and storage instructions.

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Nipol®
NITRILES

NIPOL 1312LV LIQUID RUBBER

PRODUCT SPECIFICATION
(Revised 9/26/91)

SPECIFICATION FOR NIPOL 1312LV

Nipol 1312LV is a copolymer of butadiene and acrylonitrile of medium-high oil resistance in liquid form. Sufficient non-staining antioxidant is added during manufacture for normal aging conditions. The ingredients comprising Nipol 1312LV are acceptable under FDA regulations 175.105 and 177.2600.

SPECIFICATION LIMITS

Nipol 1312LV is a viscous liquid and is amber-to-light brown in color. It shall be free from foreign material considered objectionable for normal applications.

CHEMICAL PROPERTIES

Analysis	Specification	Procedure#*
Heat Loss (%, Max.)	0.0 - 0.5	362 Hf
Ash (%, Max.)	0.0 - 0.5	873 Ba
Brookfield Viscosity cps @ Number 4 Spindle, 50°C, 12 rpm	9,000 - 16,000	170 A
Bound Acrylonitrile (%)	25.0 - 28.0	325 Ea

* Procedures available upon request.

Note: Refer to MSDS #3 for proper handling and storage instructions.

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APPENDIX L

MACH I, INC. PRODUCT LIST

APPENDIX L
MACH I, INC. PRODUCT LIST

MACH I®

Military/Aerospace Chemicals

Product List

Metal Deactivating Antioxidants	PRO-TECH® Stabilizers
Burning Rate Catalysts	NANOCAT® Superfine Iron Oxide (SFIO) NANOCAT® SFIO Dispersion in Poly bd® R45M NANOCAT® SFIO Dispersion in Plasticizer
Functional Polymers	Polybutadiene/Maleic Anhydride Adducts Polybutadiene Acrylate
Microencapsulation	Coacervation Physical Vapor Deposition Chemical Vapor Deposition CAMES™ Sensors
Carbon Fibers	Uncoated Ceramic Coated Metal Coated Polymer Coated
Specialty Metal Powders	Coated Boron Coated Magnesium Coated Aluminum
Processing Aids	**GANEX® Resins**
Ultraviolet (UV) Absorbents	NANOCAT® Superfine Iron Oxide (SFIO) NANOCAT® SFIO Dispersion in Mineral Oil NANOCAT® Superfine Titania

MACH I Inc., 340 East Church Road, King of Prussia, PA 19406 (610) 279-2340 FAX: (610) 279-6605

REFERENCES

1. Warth, A. H. *The Chemistry and Technology of Waxes;* 2nd ed.; Reinhold Publishing: New York, 1956.

2. *Encyclopedia of Explosives and Related Items;* PATR 2700, 1983; Vol. 10, pp W-20 - W-57.

3. Ablard, J. E. *HBX-1: Its History and Properties;* NAVSEA-03-TR-021, 1975.

4. Seeger, D. E. et al. *Composition B Wax Study;* Annual Meeting, Loading Section, Ammo. Technol. Div. American Defense Preparedness Assn., 1974 (by Picatinny Arsenal).

5. Kemp, R. T.; Anthony, F. *Synthesis of Waxes for the Phlegmatization of Explosives;* NSWC/DL-TR-3364, 1975.

6. Rubin, J. *Desensitization of High Explosives by Waxes;* PATR 1489, 1945.

7. O'Connor, P. et al. *Hydrocarbon Processing;* **1991**; Vol. 70, pp 76-84.

8. *Petroleum Supply Annuals*, Energy Information Administration, Office of Oil and Gas, U.S. Dept. of Energy, Washington, DC 20585, 1974-91 .

9. Hogge, W. C.; Cousins, E. R. *Evaluation of Synthetic Waxes Desensitizing Explosives;* KWSY-TR-75-3, 1975.

10. Staples, J. M. *Desensitizing Wax Qualification;* Development Report No. M-23, Holston Defense: Kingsport, TN, 1973.

11. Williamson, W. O. *J. of Applied Chemistry;* **1958**; Vol. 8, p 661.

12. Bowden, F. P.; Yoffe, A. D. *Initiation and Growth of Explosion in Liquid and Solids;* Cambridge University: 1952.

13. Frey, R. B. *Cavity Collapse In Energetic Materials;* BRL-TR-2748, July 1986.

14. Field, F. E. et al. *Deformation, Fracture and Explosive Properties of Reactive Materials;* USARDSG Technical Report 4380A-R-N, August 1988.

15. Velicky, R. W. *Effect of Additives on the Mechanical Behavior and Shock Sensitivity of Composition B;* ARAED-TR-88031, January 1989.

REFERENCES (continued)

16. Eadie, J. *The Effect of Wax on the Shock Sensitivity of Explosive Compacts;* Fourth Symposium, Naval Ordinance Lab.: White Oak, Silver Spring MD, 1965; pp 399-403.

17. Bowers, R. C.; Romans, J. B.; Zisman, W. A. *Industry, Engineering & Chemistry, Product Research and Development;* 1973; Vol. 12, p 2.

18. Harris, J. *Thermochimica Acta;* **1977**; Vol. 18, p 125.

19. Pinto, J.; Nicolaides, S.; Weigand, D. A. *Dynamic and Quasi-Static Mechanical Properties Of Comp B and TNT;* ARAED-TR-85004, November 1985.

20. Starkenberg, J.; McFadden, D. L.; Pilarski, D. L. *The Sensitivity of Several Explosives in the Launch Environment;* BRL-TR-3095, April 1990.

21. Swallowe, G. M.; Field, J. E. *Proceedings of the Royal Society London;* **1982**; Vol. A379, p 389.

22. Aubert, S. A.; Massey, S. J.; Corley, D. D. *Desensitization of Tritonal with Wax Emulsions;* AFATL-TR-88-32, July 1988.

23. Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters;* CRC: Boca Raton, FL, 1983.

24. Van Krevelen, D. W.; Hoftyzer, P. J. *Properties of Polymers, Their Estimation and Correlation with Chemical Structure;* Elsevier, NY, 1976.

25. Timmons, C. O.; Zisman, W. A. *J. of Colloid and Interface Science;* **1968**; Vol. 28, p 106.

26. ICI Specialty Chemicals Bulletin, *The HLB System;* June 1990.

27. Becher, P. *Emulsions: Theory and Practice;* Reinhold: NY, 1957.

28. Stiegerwald, M. L. *Surfactants for PBX and TNT-Based Systems, Preliminary Report of Eglin In-House Effort;* Sept. 30, 1991.

29. Taylor, R. C.; Kosowski, B. M.; Bowman, G. T.; Williams, E. M. *Viscosity Reducing Dispersants For Plastic Bonded Explosive;* 1993 JANNAF Propulsion Meeting Proceedings, Monteray CA, Nov. 1993.

30. Gaylord, N. G. *CHEMTECH;* **1989**; Vol. 19, p 435.

REFERENCES (continued)

31. ARCO Chemical Bulletin. *SMA Resins;* 1982.

32. Ricon Resins Inc., personal communications, April 19, 1993.

33. Stanton, H. D.; Reed Jr., R. (U.S. Navy), U.S. Patent 4,445,948, May 1, 1984.

34. Dagley, I. A.; Ho, S. Y. *Impact Ignition Senitiveness of RDX With Ethylene-Vinyl Acetate (EVA) Copolymers;* 22nd International Annual Conference Of ICT, Germany, July 1991.

35. *Encylopedia of Polymer Science And Technology;* Acrylic Polymers, Interscience NY, 1990.

36. Shell Bulletin, *Kraton Thermoplastic Rubber;* 1989

37. Becher, P. *J. of Colloid Science;* **1963**; Vol. 18 p 665.

38. Gergel, W. C. *Lubricant Additive Chemistry;* International Symposium of Technical Organic Additives, Interlaken, Switzerland, May 24, 1984.

39. Chemical Marketing Report; September 14, 1992.

40. Hildebrand, J. H. *J. of American Chemical Society;* **1916**; Vol. 38 p 1452.

41. Information Contained in Table 1 is a summary from the following sources:
    a. Production data - Reference 8.
    b. U.S. Imports *U.S. Imports for Consumption* U.S. Department of Commerce, Washington D.C.
    c. U.S. Exports *U.S. Exports, Schedule E, Commodity by Country* U.S. Department of Commerce, Washington D.C.