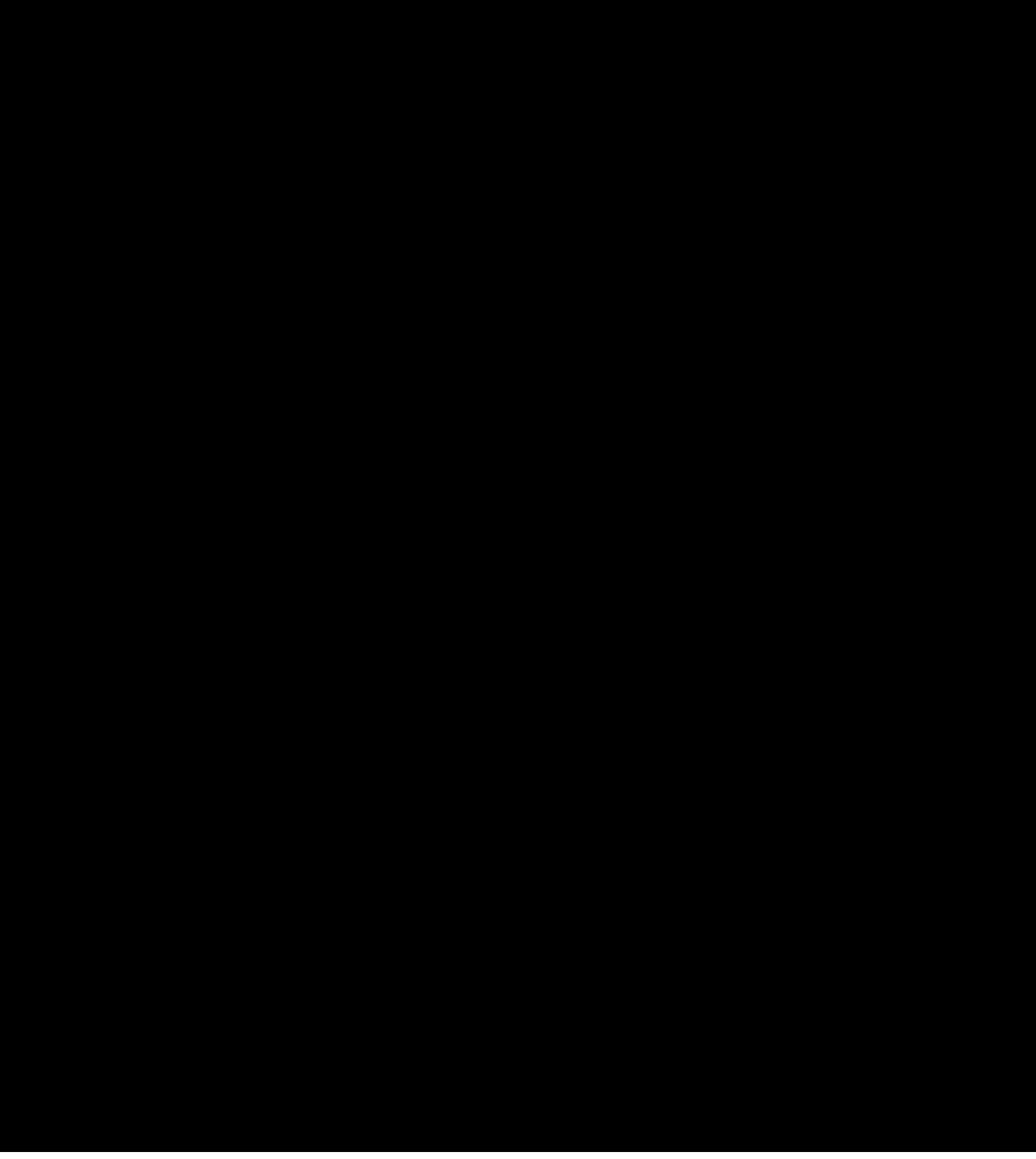




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PARLIN LABORATORY REPORT

SUBJECT:

STRIPPABLE PROTECTIVE SPRAY COATINGS
NAVY RESEARCH CONTRACT NO. 5216

PERIOD:

JANUARY 1, 1944 TO JUNE 30, 1944

NOTEBOOK:

NO. 2051

PREPARED BY:

C. G. Murphy
C. G. MURPHY

APPROVED BY:

J. P. SERMATTEI
JPS

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PARLIN LABORATORY REPORT NO. 900

**SUBJECT: STRIPPABLE PROTECTIVE SPRAY COATINGS
NAVY RESEARCH CONTRACT NORD-5216**

I - INTRODUCTION

The subject research and development project was undertaken at the request of the Bureau of Ordnance, Special Projects Section, under Navy Department Contract NORD 5216 in order to provide a sprayable strippable film for use in protecting military and naval equipment from corrosion. These films would be applied:

- (a) For initial shipment overseas by domestic manufacturers and depots.
- (b) For temporary storage and for other over-water movement in theatres of operation.
- (c) For storage of reserve stocks and replaced equipment immediately, and at the conclusion of hostilities, at various depots and in the United States.

The initial general requirements set up by the Navy for a product of this type were:

1. Provide corrosion protection to equipment covered with the film. Exposure would include humidity, rain, salt spray and sea water; temperature would vary from tropical to arctic. The film should be waterproof and should not pass more than two or three grams of water vapor per square meter per 24 hours at 100°F. and 760 mm.
2. Be applicable by spraying at room temperature by unskilled personnel.
3. Be capable of being completely stripped off the part quickly by hand in the field.
4. Bridge openings of substantial diameter.
5. Resist fungus, insect and rodent attack.
6. Have no deleterious effect on metal or wood surfaces or on paint over which it may be applied. Most of these paints are alkyd or phenolic base.

7. Remain reasonably flexible and not crack or craze on exposure to various types of atmospheres.

8. Provide a dry exterior surface.

9. Be compatible with the standard preservative oils used by the Army and Navy.

This report covers the results of six months work to develop such a product or products.

II. RESULTS AND CONCLUSIONS

From the various potential film formers investigated, sprayable, strippable protective compositions were developed based on ethyl cellulose, nitrocellulose and neoprene. The ethyl cellulose composition has the best all round combination of physical and working properties and, on the basis of data now available, is considered to be the most promising. The nitrocellulose composition is equally satisfactory in most respects, but due to its inflammability it is considered inferior to the ethyl cellulose. The neoprene composition has certain definite advantages over both the ethyl and nitrocellulose types but because it must be vulcanized to attain its optimum film properties and must also be a two package proposition, it also is considered second to the ethyl cellulose type. Detailed data on the composition and properties of the above three products can be found in the body of the report.

One of the major problems encountered in this work was to develop compositions having good initial strippability and good retention of strippability on aging. Surface active agents as a class were found to produce this effect with one particular agent, soya lecithin, being outstanding in its reduction of adhesion combined with no deleterious effect on corrosion resistance.

Early in the work with ethyl cellulose, one of the problems to overcome was that of obtaining satisfactory outdoor durability. It was found that the durability could be definitely improved to a point believed to be satisfactory by the use of a combination of an anti-oxidant and proper pigmentation. Still further improvement can be obtained by applying a topcoat of a black or dark gray flexible lacquer. Du Pont 259-023 Black "Ducco" was used in our experimental work.

III - DETAILED RESULTS AND CONCLUSIONS

A survey was made of the available film forming materials and the most likely candidates were selected for investigation.

Since a quite satisfactory hot dip strippable protective coating based on ethyl cellulose had been developed by various concerns for the Army Ordnance Department against specification AXE-1167, and because Naval Ordnance had found in their preliminary work on this problem that the most promising formulations developed at that time contained ethyl cellulose, this form former was considered the most promising candidate for initial work. Other film formers considered worthy of investigation were neoprene, butyl rubber, Buna S, "Vistanex", "Thiokol", the "Vinylites", "Butacite", "Saran", butyl isobutyl methacrylate, methyl methacrylate, nitrocellulose, cellulose acetate and nylon.

Of the above listed materials, strippable sprayable formulations were developed using ethyl cellulose, nitrocellulose, neoprene, butyl rubber, Buna S, perbunan, polyvinylbutyral and the 50/50 interpolymers of n-butyl isobutyl methacrylate. No work has yet been done on the other candidates because of their less promising characteristics or availability and in the case of the "Vinylites", to avoid duplication of the work already being done at the Naval Ordnance Laboratory at Silver Spring, Maryland.

Of the strippable, sprayable formulations developed, three show the most promise of meeting the desired requirements for a product of this type. These were based respectively on ethyl cellulose, nitrocellulose, and neoprene. The remaining formulations based on butyl rubber, Buna S, perbunan, polyvinylbutyral and the butyl isobutyl methacrylate interpolymers were found to be less promising and no further work on them is planned at the present time.

Because of the otherwise promising results obtained with nitrocellulose, a high spot evaluation of cellulose acetate-butyrate is underway to develop a less inflammable coating. No pertinent results are as yet available.

The composition having the best combination of properties for the subject purpose is based on ethyl cellulose. The present preferred formula carries the du Pont experimental code J-200-X-6463 and has the following composition:

J-200-X-6463

Ethyl Cellulose (N-type) 35cps.	8.30%	<u>Solids Composition</u>	
Raw castor Oil	2.80	Ethyl Cellulose	41.5%
Estic #44 Oil (Std. Oil of N.J.)	7.00	Raw Castor Oil	14.0
Soya lecithin	0.40	Estic #44 Oil	35.0
Phenyl-a-naphthylamine	0.10	Soya lecithin	2.0
Carbon Black	0.90	Phenyl-a-naphthylamine	0.5
Zinc Oxide	0.50	Carbon Black	4.5
Hexane	20.00	Zinc Oxide	2.5
Toluene	12.00		100.0%
Ethyl Alcohol	8.00	<u>Solvent Composition</u>	
N-butyl alcohol	12.00	Hexane	25.0%
Hi-solvency Naphtha (Union Oil #30)	28.00	Toluene	15.0
	100.00%	Ethyl Alcohol	10.0
		N-butyl "	15.0
		Union Oil #30	35.0
			100.0%

Gallon Weight = 6.89 pounds at 25°C.
Viscosity (#10 ~~viscometer~~ Cup) = 138 sec. at 25°C.
Total Solids = 20.0%
Tensile Strength = 750 - 800 lbs./sq. in.
Elongation at break = 55 - 60%
Permeability Value = 400 grams/100 sq. meters/hr. at 39.5°C.
at a film build of 8 mils
Theoretical Coverage = 263 sq. ft./gal. at 1 mil

Formulation J-200-X-6463 is reduced to 17.5% total solids for spray application with J-3000-X-6467, a thinner composed of the same solvents in the same ratio as contained in J-200-X-6463. A film build of 7 - 9 mils can be laid down in two spray applications using a pressure pot spray gun. A DeVilbiss MBO type spray gun with an FF type and a #704 "hot spray" type head is recommended when applying J-200-X-6463. A pressure of 90 pounds on the line and 20 pounds on the pot is recommended.

A film of J-200-X-6463 of 8 mils thickness will dry to handle in 3 - 5 hours and is completely dry in 24 hours at room temperature. It can then be readily stripped from steel and painted surfaces, other than the pyroxylin type.

Based on preliminary exposure data and accelerated weathering tests, outdoor durability equivalent to at least 3 to 4 months in Florida can be expected. The period of durable life can be materially extended, however, by applying a topcoat such as 259-023, Black "Duso", over the strippable coating without adversely affecting its strippability or resistance to corrosion.

No corrosion occurs on polished steel test pieces coated with J-200-X-6463 when tested under the following conditions:

Ten consecutive cycles of:

- 16 hours at 100% relative humidity at 100°F.
- 3 hours at 40°F.
- 2 hours at 160°F.
- 3 hours immersion in a 5% salt solution at 70°F.

Although J-200-X-6463 offers good protection from corrosion, its moisture vapor permeability value is considerably higher than that of moistureproof "Cellophane". In our scale (P.V. = grams/100 square meters/hour at 39.5°C. under a vapor pressure differential corresponding to 100% relative humidity on one side of the film and less than 3% on the other side), the latter has a value of 20 to 30, whereas J-200-X-6463 has a value of approximately 400 at a film build of 8 mils. (See Chart I)

The nitrocellulose stripping lacquer is considered to be less interesting than the ethyl cellulose type mainly because of its questionable inflammability. The present preferred formula carries the experimental code J-243-X-6447 and has the following composition:

J 243 X 6447

Nitrocellulose (6 Seconds)	10.00%
Trioresyl Phosphate	8.00
Estie #44 Oil (Std. Oil of N.J.)	0.60
Soya lecithin	0.40
Carbon Black	0.90
Zinc Oxide	0.50
Hexane	8.00
Acetone	19.90
Ethyl Alcohol	11.90
N-butyl	8.00
N butyl Acetate	31.80
	100.00%

Solids Composition

Nitrocellulose	49.1%
Trioresyl phosphate	39.2
Estie #44 Oil	2.9
Soya lecithin	2.0
Carbon black	4.4
Zinc Oxide	2.4
	100.0%

Solvent Composition

Hexane	10.0%
Acetone	25.0
Ethyl Alcohol	15.0
N-butyl	10.0
N-butyl Acetate	40.0
	100.0%

Gallon Weight = 7.45 lbs. at 25°C.

Viscosity (#10 Parlin Cup) = 132 second at 25°C.

Total Solids = 20.4%

Tensile Strength = 2500 - 3000 lbs./sq. in.

Elongation at break = 50 - 55%

Permeability Value = 300 grams/100 sq. meters/hr. at 39.5°C. at a build of 8 mils

Theoretical Coverage = 196 sq. ft./gal at 1 mil

Formulation J 243 X 6447 is reduced to 17.5% total solids for spraying with J 3000 X 6451, a thinner composed of the same solvents in the same ratio as contained in J 243 X 6447. A film build of 7 - 9 mils can be laid down in two spray applications using the same spray equipment and under the same conditions as recommended for the ethyl cellulose stripping lacquer.

It is also equivalent in drying speed to the ethyl cellulose stripping lacquer and is readily strippable from both bare steel and painted surfaces, other than the pyroxylin type.

Based on preliminary exposure data and considerable durability background with similar pyroxylin type formulations, J 243 X 6447 is expected to have satisfactory outdoor durability possibly being better in this respect than the ethyl cellulose type.

No corrosion occurs to polished steel test pieces coated with J-243-X-6447 when tested under the conditions previously outlined in the 10 cycle test. Moreover, J-243-X-6447 is somewhat more impermeable to moisture vapor than J-200-X-6463, having a permeability value of approximately 300 at a film build of 8 mils. (See Chart I)

Because of its better combination of tensile strength and distensibility at room temperature than the ethyl cellulose stripping lacquer, J-243-X-6447 is more easily strippable. This would probably be advantageous when stripping from irregular shaped parts. The main disadvantage of the nitrocellulose type is, of course, its inflammability. This, however, would only present a problem after the coating was stripped from the parts and it could be minimized by exercising normal care in seeing that large quantities of the stripped film were not allowed to accumulate.

The third of the most promising stripping lacquers is based on neoprene. The present preferred formula is coded J-200-X-6453 and has the following composition:

J-200-X-6453

KMR Neoprene	12.58%
Phenyl-b-naphthylamine	0.26
Stearic acid	0.26
Extra light calcined magnesia	0.52
Soft carbon black	22.01
Circle lt. process oil	1.26
Zinc oxide	0.11
Soya lecithin	0.30
di Pent #552 Accelerator	0.15*
Toluene	37.70
Industrial xylene	24.85
	<u>100.00%</u>

Solids Composition

KMR Neoprene	100.0
Phenyl-b-naphthylamine	2.0
Stearic acid	2.0
Magnesia	4.0
Soft carbon black	175.0
Circle Lt. process oil	10.0
Zinc oxide	1.0
Soya lecithin	2.0
#552 Accelerator	1.2
	<u>297.2</u>

Solvent Composition

Toluene	60.0%
Industrial xylene	40.0
	<u>100.0%</u>

*piperidinium pentaoxethylene dithiocarbamate

Gallon weight = 8.50 lbs. at 25°C.
Viscosity (#10 Parlin cup) = 16 sec. at 25°C.
Total Solids = 37.45%
**Tensile Strength = 850 - 900 lbs./sq. in.
**Modulus at 100% elongation = 300 - 350 lbs./sq. in.
**Permeability value = 50 grams/100 sq. meter/hr. at 39.5°C.
at an 8 mil film build
Theoretical Coverage = 431 sq. ft/gal. at 1 mil

Film fully vulcanized (24 hours at 150°F.)

Unlike the two preceding stripping lacquers based respectively on ethyl and nitrocellulose which dry to their final film properties by solvent evaporation, the above composition, J-200-X-6453, depends for its final film properties on vulcanization. This may either be accomplished at an elevated temperature such as in 24 hours at 150°F., or upon aging at room temperature for a period of one month to six weeks. During the air dry vulcanization period the neoprene film provides good protection from corrosion to the parts coated and is only deficient in film strength which of course reduces the ease of stripping during this period. However, it is possible to strip J-200-X-6453 from the substrate after drying only 48 hours but not nearly as easily as when the film is fully vulcanized.

Formulation J-200-X-6453 will not vulcanize as packaged. Just before using, a vulcanization accelerator and activator must be added. The immediate effect of making these additions is to cause a rapid thickening of the solution almost to the gel point. However, within two to three hours the viscosity returns to normal, at which time the solution can be applied by spraying in the same manner as outlined for J-200-X-6463, the ethyl cellulose stripping lacquer. Here again a build of 7 to 9 mils can be laid down in two applications.

It should be pointed out, however, that the stability of the activated neoprene solution is relatively short, from 50 to 100 hours. (See Chart III). Therefore, only the quantity of neoprene stripping lacquer that can be used up in this period should be activated at one time.

Formulation J-200-X-6453 dries to a substantially tack free condition in 16 hours at room temperature and as stated above will vulcanize to a tough, resilient, readily strippable film in 24 hours at 150°F. or in one month to six weeks at room temperature. If the parts coated with J-200-X-6453 are to be placed in contact with each other

within a week after being coated, they should be dusted with talc after drying 24 hours in order to prevent sticking.

Preliminary exposure tests indicate that satisfactory outdoor durability can be expected from J-200-X 6453 as panels exposed one month in Florida and for 500 hours to ultra-violet radiation show no appreciable weathering. When subjected to the ten cycle corrosion test outlined previously, steel test pieces coated with J-200-X 6453, both when started in the test cycle before vulcanization and when started fully vulcanized, show no rust or corrosion.

The neoprene stripping lacquer has a low moisture vapor permeability value at a film build of 8 mils, being definitely better in this respect than either the ethyl or nitrocellulose lacquers and only slightly inferior to moistureproof "Cellophane". On our scale, J-200-X 6453 has a permeability value of 50 grams as compared to 20-30 grams for moistureproof "Cellophane".

Although J-200-X 6453 has the disadvantage of having to be vulcanized in order to obtain the optimum film properties, and hence must have the accelerator and activator packaged and added separately, its tough, resilient, less permeable film is superior to the ethyl cellulose and nitrocellulose types in providing protection from mechanical damage, scuffing and abrasion.

In the development of the above described stripping lacquers, the following data on the various factors affecting the physical and working properties of strippable protective coatings has been obtained:

As in the case of permanent protective finishes, the working properties and protection afforded by a given film is a function of its thickness. With strippable films, in order to get ease of strippability, the film must have a total cohesive strength greater than the adhesion of the film to the substrate. The minimum film thickness necessary will vary, depending upon the tensile strength of the film in relation to its adhesion to the substratum. Tests have shown that a minimum build of 5 mils is necessary to get easy strippability with the ethyl cellulose, nitrocellulose and neoprene compositions.

The effect of film build on resistance to corrosion has also been studied and it has been found that corrosion increases as the film thickness decreases. A minimum build of 7 mils for the ethyl and nitrocellulose types is necessary

to provide adequate protection from corrosion, and that a slightly lower build of 5 mils for the neoprene type will provide the same protection. These facts correlate to some extent with the results of the effect of film build on permeability. However, the property of corrosion resistance involves factors other than moisture vapor permeability. Chart I shows that, within limits, the moisture vapor permeability of a film varies almost inversely as its film build.

It is therefore indicated that in order to obtain maximum ease of stripping, minimum permeability and good corrosion resistance a build of 7 - 9 mils is essential.

Although the durability of a stripping lacquer is affected by many factors, it was found in the work done to improve the durability of the earlier ethyl cellulose stripping lacquers, that major improvements can be obtained by (1) proper pigmentation and (2) the use of anti-oxidants such as phenyl- α -naphthylamine and the monobenzyl ether of hydroquinone. Fig. I shows the effect of the use of phenyl- α -naphthylamine, while Fig. II shows the effect of pigments on durability.

In Fig. I both panels have been exposed one month in Florida. The panel on the left is a clear ethyl cellulose stripping lacquer, consisting of ethyl cellulose 40, blown castor oil 20, and Estic #44 Oil 40. It has failed by becoming very brittle and is unstrippable. The panel on the right is the same as the other except for the addition of 0.5% phenyl- α -naphthylamine. Although it is not readily strippable and has lost some of its flexibility, it can be stripped with difficulty.

In Fig. II all panels have been exposed one month in Florida. Looking from left to right, the first panel is the clear described in the preceding paragraph, the second is the same pigmented with zinc oxide, the third with red lead, and the one on the extreme right with carbon black. All have failed except the carbon black modification, although the zinc oxide and red lead modifications are in better shape than the clear. In all cases it is only the lower three quarters of each panel that was exposed. An interesting effect is noticeable in the red lead modification in Fig. II. The red color is completely gone on the exposed portion becoming a dirty gray.

Fig. III illustrates the effect of applying a top coat over the clear composition. The panel on the right is the same as the one on the left except that 2 coats of 259 023 Black "Ducco" was applied as a topcoat. It is still easily strippable and exhibits good retention of flexibility.

Pigmentation also has a definite effect on the moisture vapor permeability of a film. Up to a certain point an increase in pigment content decreases the permeability value but beyond this point, it tends to rise again. This is particularly true in thinner films. (See Chart II).

One of the major problems connected with the subject development was in obtaining easy strippability and retention of strippability on aging. A search for a suitable stripping agent included examination of carnauba wax, petrolatum, stearic acid, aluminum stearate, a lead soap sold by the Union Oil Company of California under the name Stoprust D-1 and a variety of surface active agents.

Carnauba wax was the only material tested which did not decrease the adhesion of the stripping lacquer to the substrate. Stearic acid, zinc stearate, aluminum stearate and petrolatum improved the strippability but only under certain conditions. Stoprust D-1 and the surface active agents as a class were found to promote easy strippability, but in most cases, they also tended to promote corrosion. One surface active agent, soya lecithin, is outstanding in its capacity to decrease adhesion and rather than promote corrosion it tends to improve the corrosion resistance of the lacquer to which it is added. Stoprust D-1 also gave good strippability without promoting corrosion. Soya lecithin is a colloidal material consisting of approximately 65% phosphatides and 35% soya bean oil. It was found to be effective in ethyl cellulose, nitrocellulose, cellulose acetate butyrate, neoprene, polyvinyl butyral and methacrylate type stripping lacquers.

It is interesting to note that the Rustbans (standard preservative oils used by the Army and Navy) promote easy strippability but have a definitely deleterious effect on corrosion resistance when used in nitrocellulose and ethyl cellulose compositions. These oils are believed to contain sodium petroleum sulphonate, a surface active agent, which in itself imparts good strippability, but definitely poor corrosion resistance to a stripping lacquer.

III - EXPERIMENTAL

A. Ethyl Cellulose Stripping Lacquer

The work leading up to the development of the present preferred formula for the above compound is outlined below:

(1) Ethyl Cellulose

Ethyl cellulose is the most important ingredient in the formula because of its outstanding retention of toughness and flexibility over a wide range of temperatures.

Most of the work has been done with the following grades of ethyl cellulose: Hercules N-14, N-22, N-50 and N-100 grades (ethoxy content = 46.8 to 48.5%) and with Dow's Standard 10, 20 and 50 centipoise grades (ethoxy content = 48.5 to 49.5%). It has been determined that in order to obtain the maximum total solids at spraying viscosity consistent with good strippability, toughness and flexibility and using the present plasticizer, it is necessary for the film to contain a minimum of 41.5% ethyl cellulose with a viscosity in the range of 30 to 35 centipoises. Lower ethyl cellulose content, or ethyl cellulose having a lower viscosity, yields films with lower tensile strength and elongation and impairs the strippability. Higher ethoxy content as exemplified by Dow's Standard Ethocel in comparison with the Hercules N-type tends to lower toughness also, but this difference is rather slight. Chart IV shows the effect of ethyl cellulose viscosity and ethoxy content on the tensile strength and distensibility of a typical ethyl cellulose stripping lacquer.

(2) Plasticizers

A wide variety of plasticizers were evaluated for use in this compound. Among those investigated were:

- (a) Blown castor oil
- (b) Raw castor oil
- (c) Processed soya oil
- (d) Processed linseed oil
- (e) Nevinol
- (f) Nertex 10
- (g) Dibutyl phthalate
- (h) Hydrogenated castor oil phthalate
- (i) Two ricinoleate plasticizers (Baker's PD-16 and PD-16E)
- (j) Triresyl phosphate
- (k) di (p-tert. butyl phenyl) mono (5-tert. butyl 2-amyl) phosphate
- (l) Butyl phthalyl butyl glycolate
- (m) o and p toluene ethyl sulphonamide
- (n) Butyl stearate

Of the above, blown castor oil was unique in that it imparted satisfactory strippability without the use of a

stripping agent. Strippable films can be formulated with the remaining plasticizers with the use of a surface active type stripping agent. Raw castor oil when used in conjunction with a stripping agent such as soya lecithin has the best combination of properties judged from the standpoint of film properties, outdoor durability, corrosion resistance and availability. Blown castor oil yields a slightly better combination of tensile strength and distensibility but it is slightly poorer in resistance to ultra-violet radiations and hence would not be expected to have quite as good outdoor durability.

(3) Oils, Resins, Waxes, Etc.

(a) Estic #44, a paraffin base mineral oil supplied by Standard Oil of New Jersey has been found to give the best all round properties, yielding films with good strippability, tensile strength, distensibility and provides good corrosion resistance.

(b) Marathon Hyl #452, a naphthenic base mineral oil, yields films with satisfactory strength and distensibility and does not impair the strippability. However, corrosion tests indicate that it is inferior in this respect to Estic #44 Oil.

(c) Army and Navy Rust Inhibiting Oils

A number of rust inhibiting oils such as Rustban 347, 603 and 606, Stanorust 702, WS-543 and WS-466 have been evaluated. In general, each of these oils imparted better strippability than the Estic #44 Oil, with Rustban 606 and WX-466, Preservative Oil, being outstandingly better. However, Rustban 606, which is believed to contain a considerable percentage of sodium petroleum sulphonate, increases the moisture vapor permeability value and in corrosion tests it is definitely inferior to Estic #44 Oil, especially in the presence of acid accepting pigments such as zinc oxide, red lead and basic zinc chromate. The addition of sodium petroleum sulphonate to either Estic #44 Oil or Marathon Hyl #452 produces the same deleterious effect on permeability and corrosion resistance as does the use of Rustban 606 in the formula.

An interesting sidelight on the use of sodium petroleum sulphonate is its effect on the corrosion resistance provided by a film of either Estic #44 Oil or Marathon Hyl #452. When added to these oils in the percentage believed to be contained in Rustban 606, the oils so modified

when used directly over steel offer corrosion resistance equal to that of Rustban 606 and definitely superior to either of the unmodified oils. However, when used in ethyl cellulose coatings the effect is just the reverse.

(d) Petrolatum of various grades has also been evaluated. Although we have obtained some erratic results with petrolatum, in general it has been found to impart improved strippability and corrosion resistance to a film with a slight loss in tensile strength and distensibility. Amber Parms or Yellow Parms #4F supplied by Standard Oil of New Jersey are the two most satisfactory grades from the standpoint of compatibility, but do not appear to give enough added corrosion resistance or improved strippability to warrant their use. Amber Petrolatum supplied by L. Sonneborn & Sons, Inc. of Petrola, Pennsylvania, imparts improved strippability but has poor compatibility and does not improve the corrosion resistance enough to warrant its use.

(e) Lanolin was examined as a potential film modifier but does not appear to have any special merit, neither detracting from nor improving the characteristics of the film.

(f) Gumar MH was the only resin examined. It improved the compatibility of the other ingredients with each other, yielded good strippability, toughness and flexibility, and tended to improve the impedance to moisture vapor. However, in actual corrosion tests it had poor resistance to corrosion with the film showing a high degree of emulsification under high humidity conditions.

(g) Paraffin Wax was examined but only from an academic standpoint as formulations containing paraffin wax must be hot sprayed and dried at an elevated temperature. However, it materially lowered the permeability value and provided good protection from corrosion.

(4) Anti-oxidants

A number of anti-oxidants were evaluated for their anti-corrosion and film preserving effects among which were phenyl-alpha-naphthylamine, Agerite Alba, Agerite Resin D and Agasate Hipar. Although none appeared to give any added protection from corrosion and in some tests appeared to have a slightly deleterious effect, phenyl-alpha-naphthylamine and Agerite Alba (commercial monobenzyl-ether of hydroquinone)

definitely improve the durability of an ethyl cellulose film, with the former being slightly better in this respect than the latter. Apparently their effect is to slow down the degradation of the ethyl cellulose caused by the actinic rays of the sun in combination with oxygen from the air. Phenyl- α -naphthylamine was judged to have the most beneficial effect on outdoor durability without having any deleterious effect on corrosion resistance.

Figure I illustrates the effect of phenyl- α -naphthylamine on outdoor durability. As discussed in the early part of this report, the panel on the left is a clear ethyl cellulose film while the one on the right is the same composition plus 0.5% phenyl- α -naphthylamine. Both panels have been exposed one month in Florida.

(5) Pigments

The general effect of pigmenting this type of compound is (1) a gradual reduction in distensibility and strippability (2) no appreciable effect on tensile strength within the practical limit of pigmentation (3) an improvement in the durability and corrosion resistance and (4) a reduction in the permeability value up to a certain point beyond which further pigmentation causes the film to become more permeable. (See Chart II).

Among the pigments examined were zinc oxide, magnesium oxide, red lead, basic zinc chromate, carbon black, metallic aluminum, talc and ammonium ferre-phosphate. Formulations have been prepared with each of the above pigments which yielded films with good strippability, toughness and flexibility. Zinc oxide, magnesium oxide, red lead and basic zinc chromate have been tested for their effect on corrosion resistance and have been found to be beneficial. Carbon black apparently does not materially affect the corrosion resistance but has been found to be the best single means of improving the outdoor durability. Zinc oxide and red lead improve the durability somewhat but by themselves fail fairly rapidly (one month in Florida). Figure II shows the effect on durability of pigmenting the clear with zinc oxide, red lead and carbon black. The panels illustrated have been exposed for one month in Florida. Panel F-1 is the unpigmented lacquer. In this exposure period it has become very brittle and is unstrippable. Panels F-13, F-14 and F-15 represent the clear pigmented with zinc oxide, red lead and carbon black respectively. Although the zinc oxide and red lead modifications have not failed as badly as the clear, it can be seen from the knife scratches that both are quite brittle and do not have enough cohesive strength to be

strippable. The red lead formulation has also lost its original color with the exposed part of the panel being a dirty gray. The carbon black modification (F 15) is still readily strippable and has retained most of its original flexibility. Hence, from the standpoint of durability and corrosion resistance, the present preferred formula contains carbon black for maximum durability and a smaller amount of zinc oxide as an acid acceptor to insure good corrosion resistance.

It should be pointed out that only the lower three quarters of each panel has been exposed. This accounts for the difference in depth of shade between the top and bottom of each panel, particularly in the case of the red lead formulation.

(6) Stripping Agents

One of the major problems in this work has been the development of a means to reduce the adhesion of the stripping lacquer and the retention of this reduced adhesion on aging. Among the agents tried for this purpose were carnauba wax, stearic acid, aluminum stearate, zinc stearate, petrolatum, a lead soap manufactured by the Union Oil Company of California under the trade name Stoprust D-1, and a variety of surface-active agents representing different types. With the exception of carnauba wax, the remaining compounds were found to promote strippability when added to the lacquer in minor quantities. Stearic acid, aluminum stearate, zinc stearate and petrolatum were found to lessen the adhesion of the lacquer to the substrate only under certain conditions and in several cases erratic and seemingly contradictory results were obtained.

The surface active agents which are listed below were found as a class to have a definite effect on reducing adhesion.

- (a) Aerosol OT . . . an alkyl aryl sulphonate
- (b) Neomerpin N . . naphthalene sulphonic acid
- (c) Alex 350) . . . complex methyl esters of high
- (d) Alex 850) . . . molecular weight alcohols, acids and lactones
- (e) Yelkin TTS . . . oil soluble organic phosphatide
- (f) Ultramate No. 2 . . sodium petroleum sulphonate

Several other surface active agents were tested and found to be incompatible.

The first of these agents tested was Ultramate No. 2, which is reported to be the anti-corroderent agent used in the Rustbans. Ultramate No. 2 definitely lowered the adhesion to equal that obtained when Rustban 606 was used in place of Estic #44 Oil, caused an increase in the permeability value and had a definitely deleterious effect on corrosion resistance. Yelkin TTS soya lecithin, was then tried and found not only to decrease the adhesion equal to that effected by Ultramate No. 2, but at the same time tended to increase resistance to corrosion. This was also found to be true of Stoprust D-1. Tests indicate that the optimum amount of soya lecithin is 2% of the vehicle solids.

The use of a stripping agent such as soya lecithin which will not only decrease adhesion but will promote corrosion resistance is valuable not only from this standpoint but it allows (1) a wider choice of plasticizer, as blown castor oil was the only plasticizer found that could be used without a stripping agent, (2) higher pigmentation to get maximum durability and (3) less increase in adhesion on aging.

(7) Solvents

The solvent mixture used is designed to have the optimum solvency to provide the minimum viscosity at the maximum solids and to be fast evaporating enough to allow a heavy build to be applied without sagging and without trapping air bubbles in the film. The following mixture is now used: hexane (25%), telzene (15%), ethyl alcohol (10%), butyl alcohol (15%) and a medium high boiling, high solvency naphtha which corresponds to Union Oil #30 (35%). However, under adverse spraying conditions, it may be necessary to make some adjustment in this mixture. Hence a retarder, J-3000-X-6468, consisting of 25 parts butyl alcohol and 75 parts Union Oil #30 is recommended to make this adjustment.

(8) Application

Work to date to determine the optimum spraying conditions to obtain the maximum build in the minimum number of coats indicates that:

(1) The optimum spraying viscosity is 70 to 80 seconds in a #10 Farlin cup at 25°C. Higher viscosity causes bubbling while lower viscosity increases the number of coats to obtain the desired film build. (2) The air pressure at the gun should be as high as practical, preferably above 80 pounds and as near to 100 pounds as possible. Lower line pressure causes bubbling by not producing a fine enough atomization of the lacquer. (3) The pot pressure

should be between 20 and 25 pounds. Higher pressure forces more material through the spray gun so that poorer atomization takes place.

All of the above recommendations are based on the use of Devilbiss spray equipment, using a type MBO spray gun fitted with an FF tip and a "hot spray" type head #704. Although other types of heads and tips may be used, the above yield the maximum build in the minimum number of coats without entrapment of air bubbles.

Other types of spray equipment can undoubtedly be used but the conditions of application would probably have to be changed somewhat.

Under the above recommended conditions for spraying, a dry film build of 4 mils can be laid down on a vertical panel by continuous spray application before sagging begins, and without trapping any air bubbles. Another application of 4 mils can be made within one half hour after the first.

Although the present preferred formula for J-200 X-6463, ethyl cellulose stripping lacquer, represents the best composition we have been able to develop based on the work covered and may represent the optimum percentages of the most desirable components, further work is necessary to determine the best method of manufacture. In order to obtain the maximum durability from the present composition, it is planned to study the various methods of dispersing the pigments, this factor being known to have a definite effect on outdoor durability.

B. Nitrocellulose Stripping Lacquer

The work leading up to the development of the present preferred formula for the above compounds is outlined below.

(1) Nitrocellulose

Nitrocellulose with a viscosity of six seconds was chosen for this work in order to combine maximum gloss with the maximum solids at spraying viscosity. This viscosity also corresponds very closely to the viscosity of the ethyl cellulose blend, namely 35 centipoises.

(2) Plasticizers

The following plasticizers were evaluated:

- (a) Tricresyl phosphate
- (b) Dibutyl phthalate
- (c) Hydrogenated castor oil phthalate
- (d) Raw castor oil
- (e) Blew castor oil
- (f) Brown cottonseed oil

Of these, dibutyl phthalate, hydrogenated castor oil phthalate and tricresyl phosphate gave films with the least adhesion and had the best compatibility with mineral oil. Due to the non inflammability, non volatility and the good combination of flexibility and toughness that tricresyl phosphate imparts to nitrocellulose compositions, this plasticizer was selected.

(3) Oils and Resins etc.

Based on the work done on the ethyl cellulose development and to obtain the optimum flexibility at low temperatures combined with lack of thermoplasticity at high temperatures, no resin is contained in this composition. Based on the background gained in the development of the ethyl cellulose composition Estic #44 was selected as the oil. The nitrocellulose composition cannot, however, tolerate the amount of oil that the ethyl cellulose type can (3% versus 37.6%).

(4) Anti Oxidants

Although anti oxidants such as phenyl- α naphthylamine and Agerite Alba were tried, there were some indications that they promoted corrosion. Therefore, the nitrocellulose stripping lacquer contains none.

(5) Pigments

Based on the background developed for pigmenting the ethyl cellulose stripping lacquer, on corrosion and preliminary durability tests carbon black and zinc oxide were selected.

(6) Stripping Agents

Because of the good adhesion of the nitrocellulose stripping lacquer regardless of the plasticizer used, a stripping agent is essential.

The following compounds were tested for their effect on strippability:

- (a) Petrolatum
- (b) Stearic Acid
- (c) Zinc stearate
- (d) Aluminum stearate
- (e) Carnauba Wax
- (f) Ultramate #2
- (g) Soya lecithin

None of the above gave the desired degree of strippability except Ultramate #2 and soya lecithin. The former, as in the ethyl cellulose composition, had a deleterious effect on corrosion resistance while the latter tended to promote corrosion resistance.

Tests indicate that 2% soya lecithin on the solid vehicle is optimum.

(7) Solvents

Again, as in the ethyl cellulose composition, the same general principles were used to formulate the solvent composition. Based on laboratory tests the present preferred composition is hexane (10%), acetone (25%), ethyl alcohol (15%), n butyl alcohol (10%), and n butyl acetate (40%).

For adverse spraying conditions a retarder J 3000 X 6452, composed of 80 parts n butyl acetate and 20 parts n butyl alcohol is recommended for the reducer.

(8) Application

The same conditions of application are recommended for the nitrocellulose lacquer as for the ethyl cellulose; namely, a DeVilbiss type MEC gun, #704 head, FF tip with an air pressure of 90 pounds on the line and a pot pressure of 20-25 pounds. The optimum spraying viscosity is 0.80 seconds in a Parlan #10 cup.

When applied under these conditions a dry film build of 7-9 mils can be laid down in two applications, applying the second one half hour after the first.

Further work on the nitrocellulose stripping lacquer for the present will be confined to establishing the best method of manufacture to insure the maximum outdoor durability.

C. Neoprene Stripping Lacquer

A modification of a neoprene paint developed by the Rubber Chemicals Division of the du Pont Company was used as

the basic formulation in the following work done in developing a strippable sprayable coating. This product had provided good protection from corrosion in a previous evaluation made by this laboratory and had exhibited poor adhesion to steel.

(1) Neoprene

The neoprene used in this composition is the KNR grade, KNR Neoprene, while being chemical similar to the other types and like them has good resistance to oils and gasoline in the vulcanized state, is better adapted to this purpose for the following reasons:

(1) It gives lower solution viscosities, permitting higher solids at spraying viscosities.

(2) By the use of suitable accelerators and activators it can be vulcanized faster than the other types at lower temperatures and without applied pressure.

(2) Pigmentation

As in the case of natural rubber, the best reinforcing agents for KNR Neoprene are the carbon blacks. Of these ordinarily used, channel black, semi-reinforcing black and soft black (Thermax), the latter gives the maximum water resistance consistent with good tensile strength, resiliency and abrasion resistance.

Laboratory tests indicate that 1/5 parts of Thermax per 100 parts of neoprene is optimum. Smaller amounts of Thermax increase the tack of the film during the vulcanization period and tend to lower the water resistance. Larger amounts decrease the distensibility and tensile strength.

(3) Modifiers

Various modifiers are included in the formula for specific purposes:

(a) Magnesia and Zinc Oxide

Magnesia (extra light calcined) is a very important neoprene compounding ingredient. When used in conjunction with zinc oxide, it performs a threefold function.

(1) It has the effect of increasing modulus of elasticity and tensile strength of the vulcanized film.

(2) It retards scorching during mixing and processing.

(3) It neutralizes any small quantities of hydrogen chloride that may be evolved during the vulcanization period or when the films are exposed to sunlight or other severely oxidizing conditions.

Zinc oxide when used in conjunction with magnesia improves the physical properties of the vulcanized neoprene. Alone it is not practical since it causes scorching and premature vulcanization.

Based on the neoprene 1% zinc oxide and 4% magnesia are considered to be optimum.

(b) Neozone D

Neozone D (phenyl-beta-naphthylamine) is used as a stabilizer of the unvulcanized compounds and as an anti-oxidant in the vulcanized film.

(c) Oil

The oil used, Circo Light Process Oil, which is a high solveny petroleum derived oil, acts as a softener for the neoprene. It improves the flexibility at lower temperatures but tends to decrease the resistance to gas diffusion.

(d) Stearic Acid

Stearic acid has a threefold effect on the neoprene stripping lacquer:

(1) It acts as an aid in processing, preventing the neoprene stock from sticking to the rolls.

(2) It reduces the time for the sprayed film to come to the tack free stage due to its blooming to the surface.

(3) It decreases the adhesion, making a more easily strippable film.

No deleterious effect on film properties or stability has been found. Tests indicate that 2% stearic acid based on the neoprene is optimum.

(c) Soya Lecithin

Soya lecithin is used in the neoprene composition to promote stripping. Tests indicate that 2% soya lecithin on the neoprene is the optimum amount. No deleterious effect on film properties, solution stability or vulcanization is obtained from its use.

(4) Vulcanization

As discussed in a previous section of this report, unlike the ethyl cellulose and nitrocellulose types of stripping lacquer, which dry by evaporation of the solvents, the neoprene stripping lacquer must be vulcanized by the addition of a vulcanization accelerator and activator. The sprayed parts are allowed to dry 16 to 24 hours in order that all the solvents are eliminated and then can be vulcanized in 24 hours at 150°F. or in about one month to six weeks at room temperature.

The films do not reach their optimum physical properties and strippability until fully vulcanized, but enough vulcanization takes place in 48 hours at room temperature so that the films are strippable with difficulty. However, during the air dry vulcanization period good resistance to corrosion is provided.

The addition of vulcanization accelerators and activators to the neoprene solution as packaged causes an immediate thickening of the solution which approaches the gelation point. However, after one-half to an hour the viscosity begins to return to normal and at the end of 2 to 3 hours is back to a normal spraying range for neoprene (50-75 sec. in a Parlin #10 cup). The solution remains stable for only a relatively short time of 50 to 100 hours. (See Chart III). However, even before the solution reaches a viscosity above the spraying range, a dropping of in good sprayability is encountered with the solution showing stringiness on spraying. This condition begins to occur between 24 and 48 hours after the addition of the activator and accelerator.

In order to obtain the fastest room temperature vulcanization consistent with the maximum solution stability, a careful balance of accelerators has been worked out. It has been found that 1.2% Accelerator 552 (piperidinium pentamethylene dithiocarbamate) and 4% Accelerator 833 (a butyraldehyde monobutylamine condensation product) based

on the neoprene gave the optimum results. Larger amounts of Accelerator 552 which also acts as a chemical plasticizer for the neoprene and as a solution stabilizer, slow up the vulcanization rate and increase the stability of the activated neoprene solution while smaller amounts have the reverse effect. Smaller amounts of Accelerator 833 slow up the vulcanization rate and hence favor solution stability while larger amounts do not appear to have any appreciable effect in either direction. Nine parts of a 50% litharge slurry in xylene are used with each part of Accelerator 833 to improve the action of the latter.

Since a mixture of one part Accelerator 833 and nine parts litharge slurry loses its potency in approximately one month, it will be necessary to package each separately. This should not present an insurmountable problem, however, as the exact amounts of Accelerator 833 and litharge slurry needed to activate any given unit quantity of neoprene solution could be packaged.

It should be pointed out that the results discussed above were obtained from work done on one lot of neoprene. Although the conclusions drawn are the results of a number of carefully run tests and are believed to be reliable, the present unavoidable variation between batches of neoprene require that several lots of neoprene be evaluated along the same lines before positive conclusions can be drawn.

(5) Solvents

Using the same general principles as were used in the ethyl and nitrocellulose type stripping lacquers to formulate the solvent composition, the present preferred combination is as follows: toluene (60%) industrial xylene (40%).

(6) Application

The recommended conditions for spraying the ethyl cellulose and nitrocellulose compositions are also applicable to the neoprene. When applied under these conditions 7 - 9 mils can be laid down in two application with a half hour wait between applications.

For adverse spraying conditions industrial xylene is recommended as a retarder.

No further work is planned on the neoprene stripping lacquer until the results of the field test on J-200 X-6453 point the way.

D. Butyl Rubber

A high spot evaluation of butyl rubber as a strippable protective coating was made because of its high degree of impermeability to gases, its excellent resistance to cracking at low temperatures and its excellent aging properties, having the broadest plateau in its curing curve of any of the other synthetic rubbers.

The examination of butyl rubber for the purpose indicated that it was inferior to neoprene in the following respects:

(1) It yields lower solids at spraying viscosity (18.0%) as compared to 37.5% for neoprene, making it necessary to apply more coats to get the same film build.

(2) It coagulates on spraying, making it more difficult to apply. With a slow enough solvent mixture, however, the film will coalesce to a continuous film.

(3) During the drying period it tends to trap bubbles in the film, due to its excellent impermeability. To overcome this it would be necessary to apply very thin coats so that more than two applications are necessary to get the minimum film build.

(4) It will not vulcanize sufficiently at room temperature to yield films with enough cohesive strength to be stripped. When vulcanized for 3 hours at 250°F., the films are strippable with difficulty, being still quite tender.

It does, however, provide good corrosion resistance to coated parts even in the unvulcanized state.

E. Perbunan

A high spot evaluation of perbunan indicates that it does not have much promise as a strippable protective coating.

Perbunan has the following desirable characteristics:

(1) Films of perbunan arrive at the completely tack-free state as soon as the solvents are evaporated and (2) when allowed to air dry, its adhesion to steel is very poor, stripping very easily from the substratum in as little as 6 - 8 hours after application.

It, however, has the following properties which makes it less desirable than neoprene as a strippable protective coating:

(1) It yields lower solids at spraying viscosity (18.0%) as compared to 37.5% for neoprene, making it necessary to apply more coats to get the same build.

(2) It cobbles on spraying making it more difficult to apply. With a slow enough solvent mixture, however, it will coalesce to a continuous film.

(3) It will not vulcanize sufficiently at room temperature to develop desirable film properties, with the unvulcanized film providing poor protection from corrosion to the parts on which it is coated.

(4) It is definitely inferior to neoprene in moisture vapor permeability after air dry vulcanization. (See Chart I).

F. Buna S

This copolymer does not appear to have any advantages over neoprene as a strippable protective coating, and has the following disadvantages:

(1) It yields lower total solids (18%) at spray viscosity than neoprene (37.5%).

(2) Cobble on spraying but coalesces to a continuous film if slow enough solvents are used.

(3) Air dry vulcanizates have poor adhesion to steel but have weak films with very little tensile strength.

G. Polyvinyl Butyral

An evaluation of polyvinyl butyral as a film former in strippable protective coatings for the subject purpose indicates that it has some outstanding properties but that its disadvantages make it less desirable than the ethyl cellulose, nitrocellulose and neoprene types.

Its one outstanding advantage is the tough, distensible film it provides. When plasticized to have a tensile strength of approximately 5000 pounds/sq. inch it has a distensibility of 130% at the break. Nitrocellulose compositions with a tensile strength of 5000 pounds/sq. inch have only an elongation of 40% at the break. The preferred formula for polyvinylbutyral has a tensile strength of 3170 pounds/sq. inch and an elongation at break of 350.0%.

Polyvinyl butyral compositions can be made to give good protection from corrosion and to have satisfactory stripping.

The main disadvantages of polyvinylbutyral are in its application. Total solids in the range of 10-12 percent are maximum due to the cobwebbing encountered on spraying. This allows only very thin films to be applied at one time. This situation is aggravated because of the slow solvents necessary to keep cobwebbing on spraying to a minimum even at such low total solids.

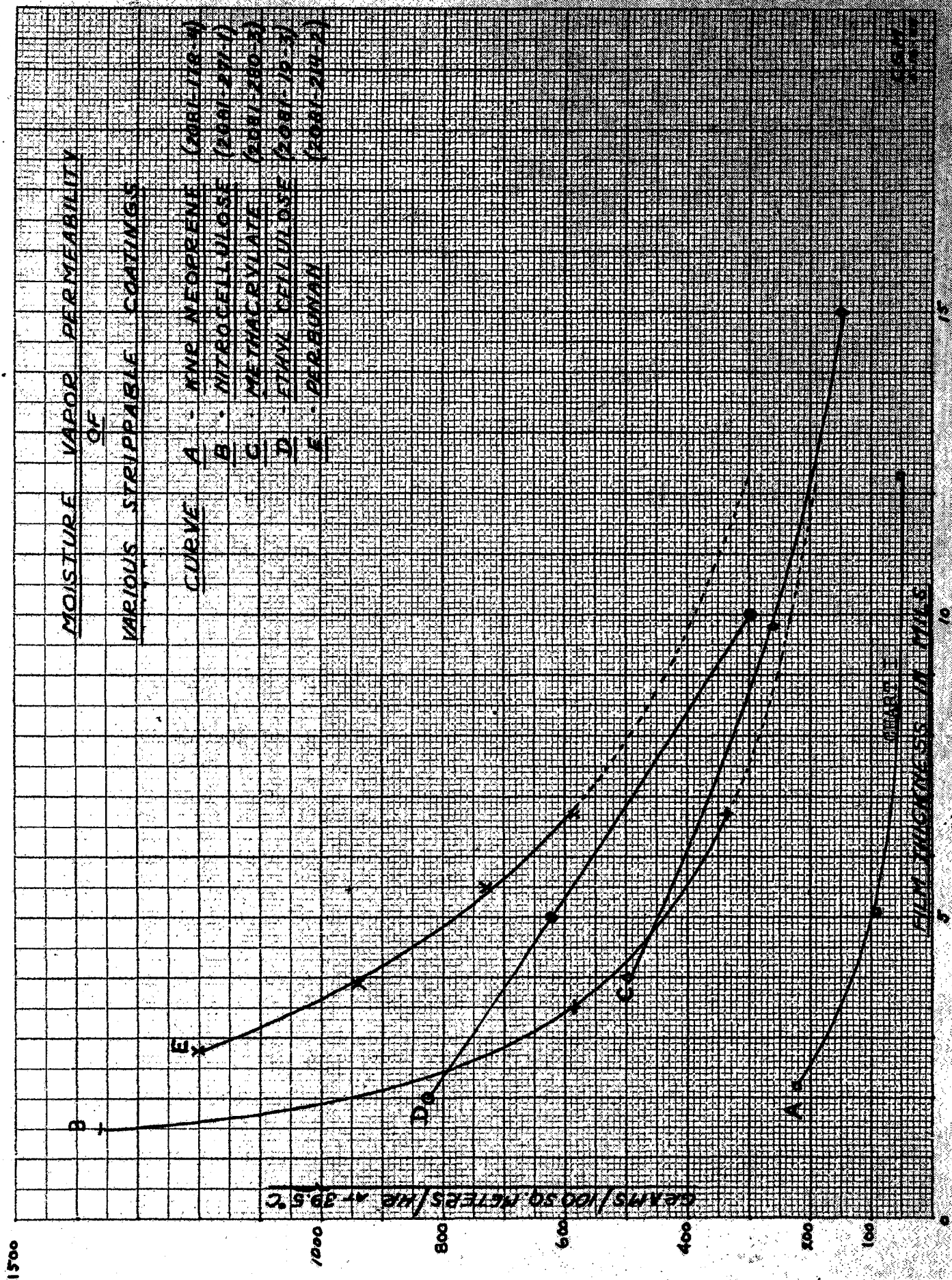
H. N Butyl Isobutyl Methacrylate

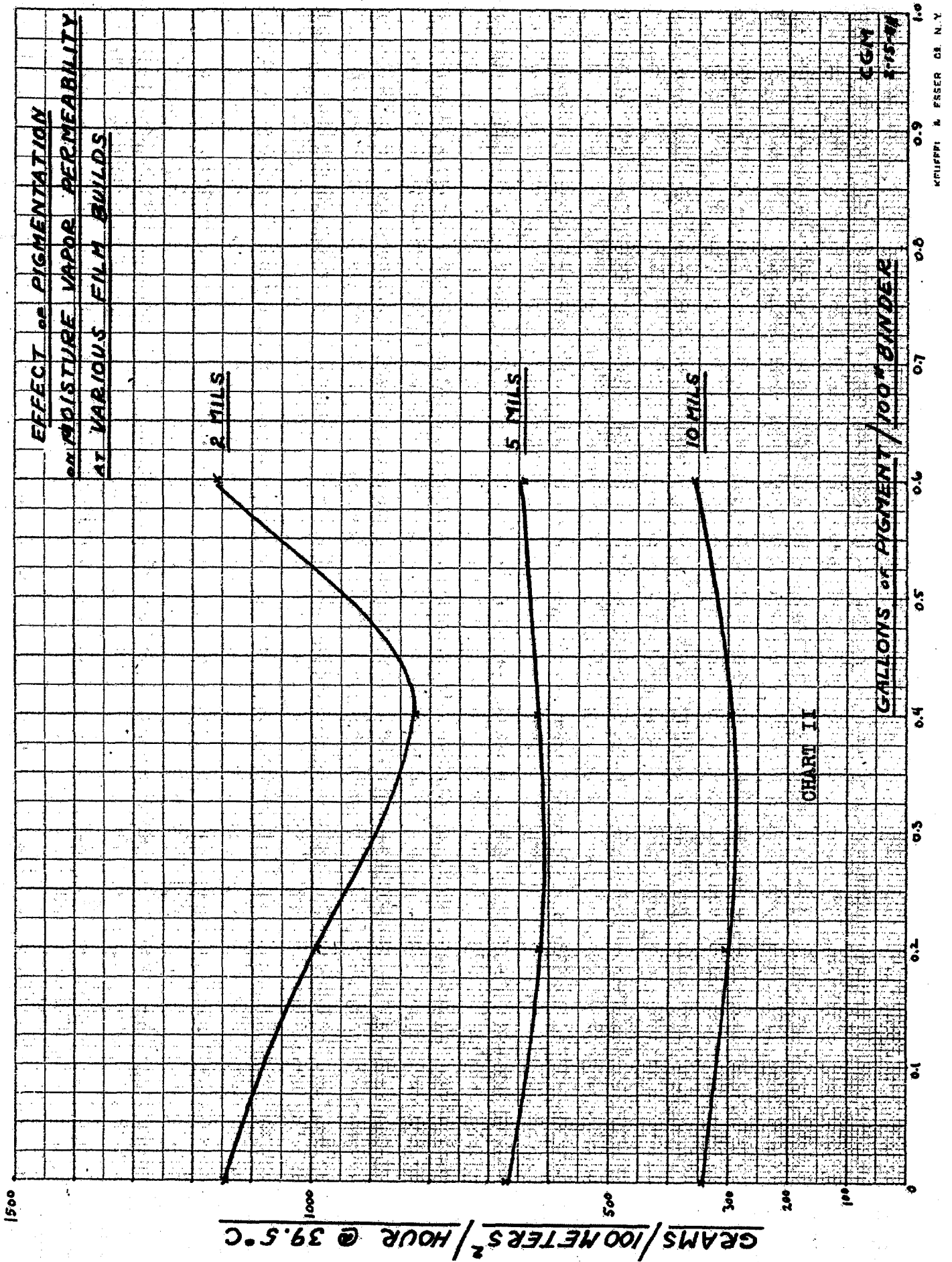
A sprayable, initially strippable lacquer was formulated with the above interpolymer. However, like polyvinylbutyral its main disadvantage is in application. Due to its poor spraying properties, which are characterized by cobwebbing, only a very thin film can be laid down in one application.

On aging 2 weeks at 150°F. the film gains enough in adhesion to be non strippable, even though it contains soy lecithin as the stripping agent. This is thought to be due to the thermoplasticity of this composition at 150°C.

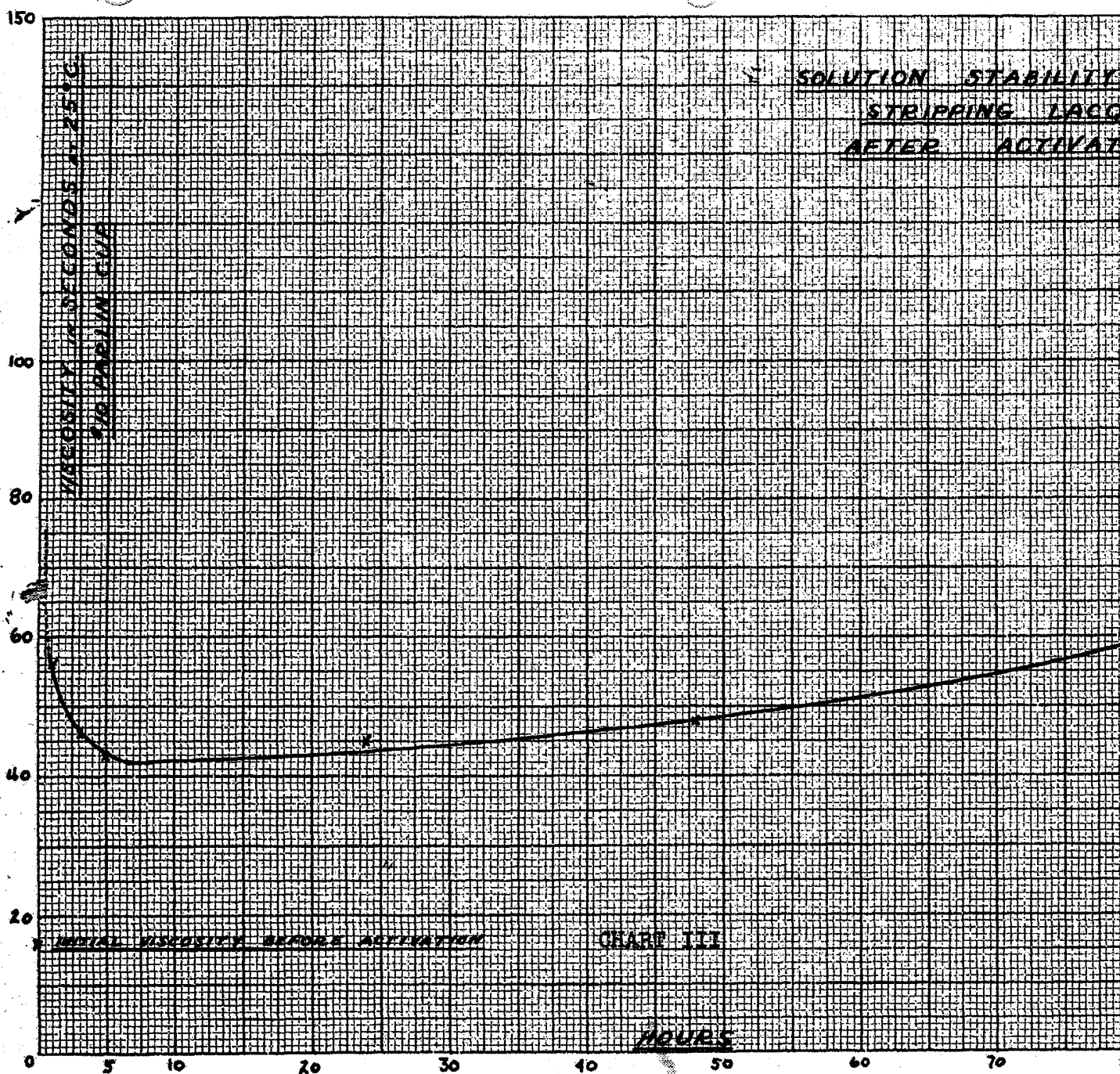
Although nothing is known at the present time of the protection from corrosion it may provide, its moisture vapor permeability conforms very closely to that of the ethyl and nitrocellulose compositions (See Chart I).

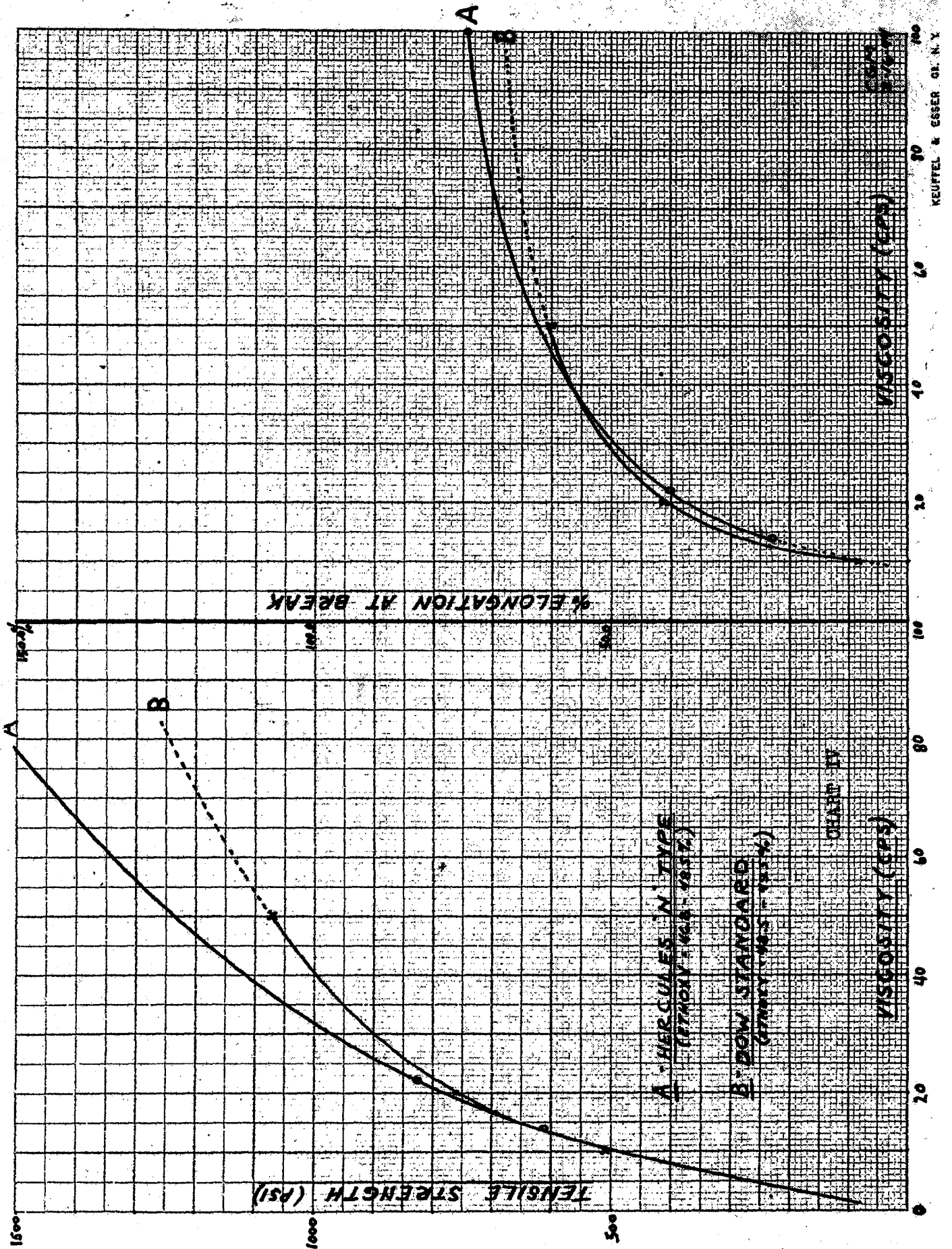
CGM:EM
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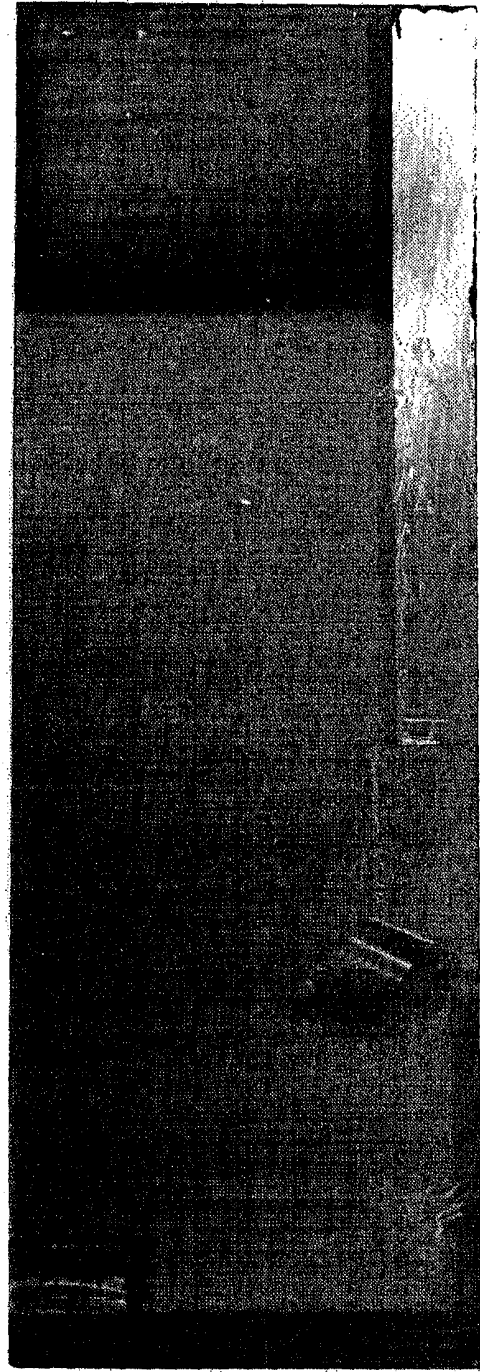
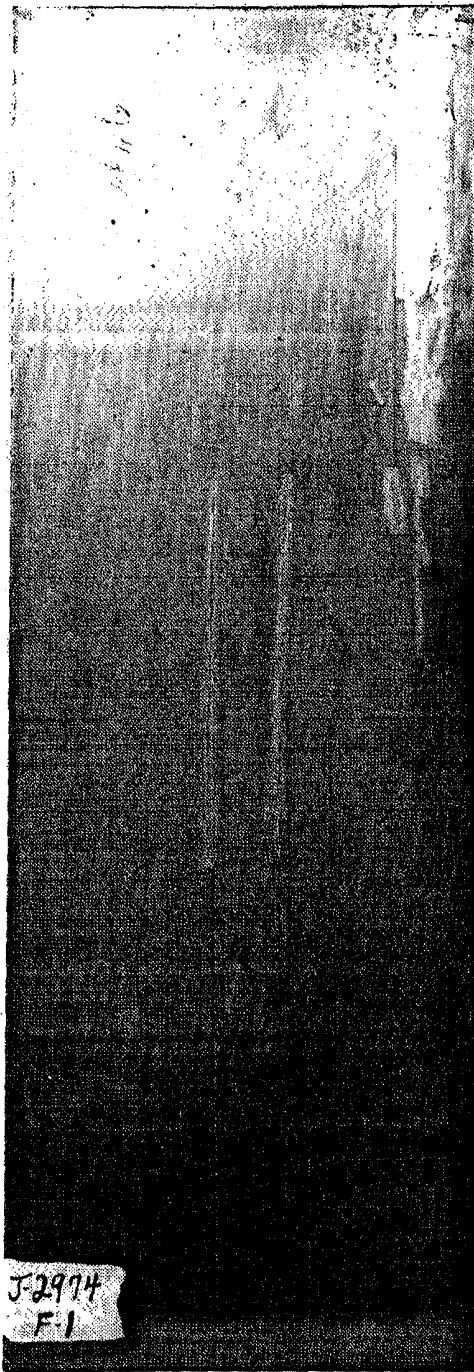


FIGURE 1

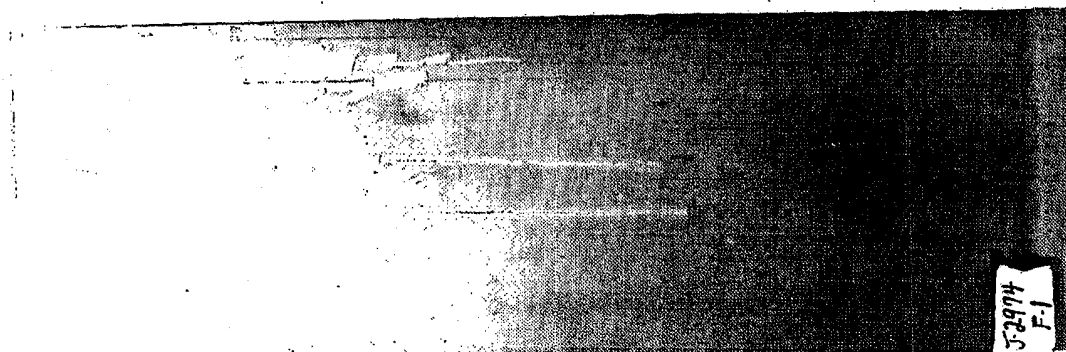
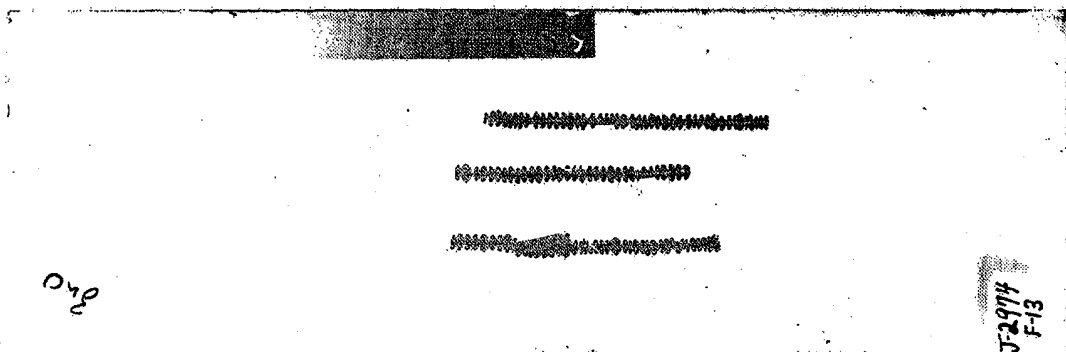
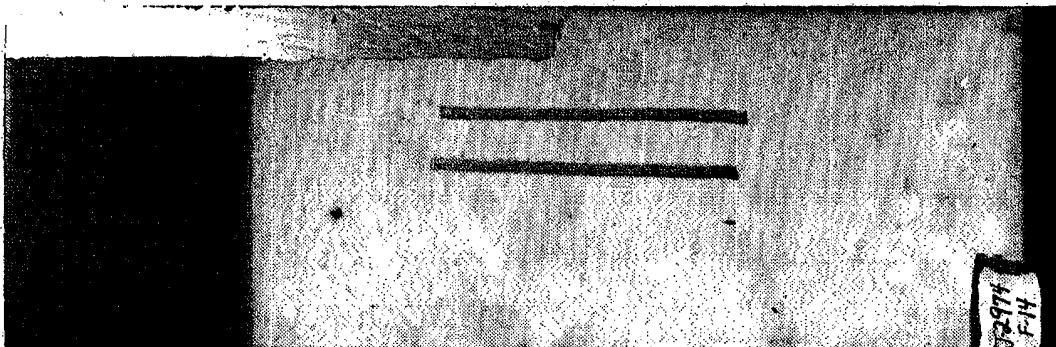
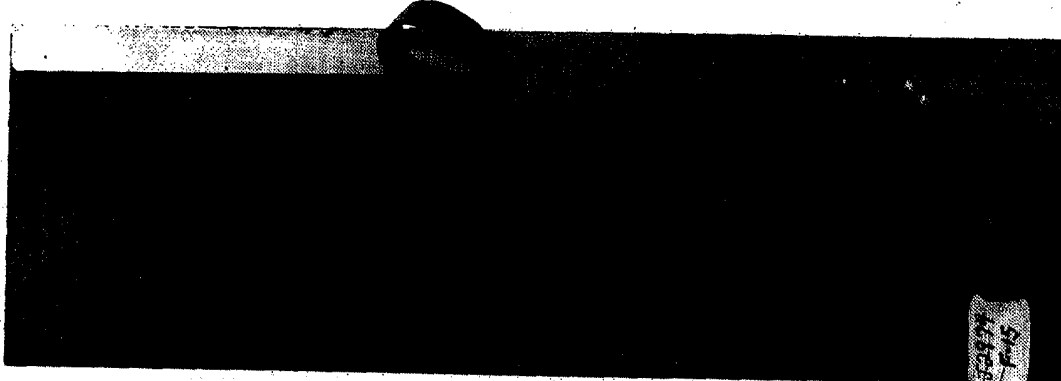


FIGURE II



FIGURE III

