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PARLIN LABORATORY REPORT

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

PERIOD: JULY 1, 1944 TO JUNE 30, 1945

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PARLIN LABORATORY REPORT NO. 906

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

I - INTRODUCTION

This report covers the results of the experimental work done under the subject research contract for the period July 1, 1944 to June 30, 1945. It supplements Parlin Laboratory Report No. 900 which covered the initial experimental work done on this problem from January 1, 1944 through June 30, 1944.

In the first phase of this work as covered in Report No. 900, an investigation was made of the most likely candidates among the then available film formers (with the exception of the "Vinylites") from which a strippable sprayable protective coating could be formulated. Investigation of the "Vinylites" was not undertaken at that time in order to avoid duplication of the work being done at the Naval Ordnance Laboratory at Silver Spring, Maryland. In this first phase of the work, the following film formers were investigated: ethyl cellulose, nitrocellulose, cellulose aceto-butyrates, neoprene, Buna S, Buna N, butyl rubber, polyvinylbutyral, and the 50/50 interpolymer of n-butyl isobutyl methacrylate. Of these, sprayable strippable protective coatings were developed based on ethyl cellulose, nitrocellulose and neoprene, all of which showed promise of meeting the general requirements for coatings of this type.

This report covers the results of experimental work done along the following lines:

- (1) Field testing of the ethyl cellulose, nitrocellulose and neoprene type coatings.
- (2) General evaluation of the "Vinylite" resins for use in strippable sprayable coatings.
- (3) Improvement in the durability of NOL-193 lacquer meeting Specification OS-3602.
- (4) Development of adhesives to adhere vinyl and neoprene type strippable coatings to steel.
- (5) Evaluation of the ingredients used in formulating NOL-193 stripping lacquer.
- (6) Development of a dipping type vinyl stripping lacquer.

II - RESULTS AND CONCLUSIONS

As a result of further laboratory work in studying the "Vinylite" resin as the main film formers in sprayable strippable protective coatings and of field tests conducted on the ethyl cellulose and neoprene types, it is felt that the vinyl resins (chloro-acetate copolymers) offer the most promise in formulating such coatings for most purposes, and especially in cases where a combination of toughness, corrosion resistance, durability and a low moisture vapor transmission rate is desired. The selection of the grade of resin, type of plasticizer and other modifiers is dependent on the use to which the coating is to be put.

For the main purpose which Naval Ordnance is proposing to use such coatings, the formulation known as NOL SS-193 (Specification OS-3602) developed by Lt. Wm. H. Holst and his group at the Silver Spring Naval Ordnance Laboratory is felt to have the best combination of properties with the possible exception of durability. A modification of this formulation in which a more soluble resin (VYNS) is used in place of a difficultly soluble resin (VYNL) is thought to have some advantages over NOL SS-193 with only a minor sacrifice in film properties. These advantages are in ease of manufacture, higher solids at spraying viscosity, and in better solution stability. Such a composition, known under the duPont experimental code J-1300-X-7147, is being field tested by the Navy at the present time.

Exposure tests indicate that the outdoor durability of both NOL SS-193 and J-1300-X-7147 can be definitely improved by pigmentation with carbon black. Other pigments and pigment combinations can undoubtedly be used to improve the durability. Exposure studies covering such potential pigment combinations are now underway. There is evidence to indicate that sufficient durability for most purposes may be obtained by using a pigmented composition only as the final topcoat. Exposure tests are also underway to determine the minimum thickness of pigmented topcoat which will be required.

From the exposure tests already examined some information on the relative durability of stripping lacquers based on various film formers is available. These tests indicate that they may be listed in the following order of increasing durability; viz., ethyl cellulose, nitrocellulose and neoprene, vinyl. The best ethyl cellulose composition we have been able to formulate has a durability equivalent to four months in Florida, the neoprene and nitrocellulose types have a durability equivalent to at least one year and probably longer in Florida, while the vinyl types are expected to be slightly superior to both the neoprene and nitrocellulose. Because

these compositions are stripping lacquers and failure is considered to occur when the film is too brittle to be stripped from a 4x12" panel in one piece, these life expectancies represent a higher order of durability than would be expected from permanent finishes.

The above conclusions are drawn from films in the range of 8-12 mils thickness so that in the case of the NOL SS-193 type application where the film thickness is on the order of 30-40 mils, considerably longer useful life can be expected.

For uses other than that of bridging openings and enveloping irregular pieces of equipment and for use where the protective film comes in direct contact with the equipment to be protected, several other vinyl type coatings have been developed. These compositions have lower tensile strength than the NOL SS-193 type, but at the same film thickness are equivalent in corrosion resistance, moisture vapor transmission rate and durability. Two typical compositions are known under the duPont experimental codes J-200-X-7012 and J-200-X-7182. They vary from the NOL SS-193 formula mainly in that they contain polymers of lower molecular weight and lower vinyl chloride content. The advantage of using such resins lies in their better solubility which yields higher solids at spraying viscosity and better sprayability. Their disadvantages are that they are not quite as tough and do not have quite as good cold-crack resistance. It is felt, however, that they are as good as it is necessary to have them in these respects.

For the NOL SS-193 type of formulation the present solvent used (methyl ethyl ketone) appears to be satisfactory for most conditions of application. However, it may be desirable to use a small amount of methyl isobutyl ketone where the application is made under conditions of extremely high humidity and high temperature. Other solvent combinations are being investigated and preliminary results indicate that acetone/toluene/methyl isobutyl ketone and toluene/methyl ethyl ketone mixtures hold some promise. In the J-200-X-7012 type of formulation a slower solvent combination is recommended as freedom from bubbling in the film is of more importance as a considerably thinner film is applied (10-15 mils).

Diethyl phthalate appears to have the best combination of properties when used as the plasticizer, but for some applications, such as in the J-200-X-7012 type, tricresyl phosphate can be used. Rustban 603 seems to be more satisfactory than an ordinary refined mineral oil such as Fractol or Estic #44 (Standard Oil of N.J.). This is particularly true in the NOL SS-193 type of formulation.

4.

Two organic compounds, Stabilizer A and Salol, were evaluated in the clear formulations for their stabilizing effect against heat and light in order to improve the durability of the clear films. Stabilizer A, the monoglyceride of a vegetable source of fatty acid manufactured by B.F. Goodrich, gave only a very slight improvement in durability, while Salol (phenyl salicylate obtained from Fisher Scientific Co.) was only very slightly better than Stabilizer A. This improvement was evidenced by slightly less darkening of the film at the end of two months' exposure in Florida and was a very minor improvement as compared to the effect of pigmentation.

Preliminary laboratory tests indicate that a cold dip vinyl stripping lacquer may have some advantages over the cold spray type or a hot melt type such as the ethyl cellulose hot melt developed for Army Ordnance (Specification ANC-117-A). Formulation J-200-X-7012 referred to above, has been recommended for this purpose and is now undergoing tests at the Naval Ordnance Laboratory, Silver Spring, Md.

Considerable search and experimentation indicates that the most satisfactory adhesive for use in adhering the NOL SS-193 type of film to the base of equipment to be protected is a phenol-formaldehyde modified butadiene/acrylonitrile type as represented by "Gaytex" or "Pliobond". Although this type of adhesive is somewhat thermoplastic and it would be desirable to use an adhesive which would convert on aging to the non-thermoplastic state, tests indicate that "Gaytex" or "Pliobond" may be adequate for the intended purpose. Preliminary work to develop a self-converting type of adhesive has as yet met with no success. However, laboratory tests indicate that there are two means of improving the resistance of a "Pliobond" bond to loosening under a load at elevated temperatures. The use of Estic #44 oil in the NOL SS-193 formula definitely improves the resistance to failure at elevated temperatures, and the deletion of VYNL resin from the NOL SS-193 also gives a slight improvement.

For adhering the neoprene type stripping lacquer to steel, the problem is more simple. Fairprene Cement #5115 (duPont Company) gives bonds which appear to be satisfactory. However, stronger bonds can be obtained with a chlorinated rubber cement such as Fairprene #5104 or an experimental cement such as J-N-205-12 also made by duPont.

In the previous report (No. 900) the use of small quantities of surface active agents such as sodium petroleum sulphonate and soya lecithin was discussed with respect to

their influence in reducing the adhesion of the stripping lacquers discussed therein. Some further work along the line of obtaining "controlled adhesion" in the vinyl type stripping lacquer has been done.

Normally the vinyl chloro-acetate resins yield stripping lacquers with very poor adhesion to most substrates and in some applications it is necessary to increase the adhesion so that the film will not be stripped from the substrate by the wind when the film is accidentally ruptured. It has been found that "Vinylite" VMCH (believed to be a vinyl chloro-acetate interpolymers with which a small amount of maleic acid has been copolymerized) can be added to a vinyl stripping lacquer to give any desired degree of adhesion. This effect is obtained, however, only in the absence of a surface active agent such as soya lecithin or sodium petroleum sulphonate as tests show that when both are used the latter are more effective in reducing adhesion than VMCH is in increasing it.

In this connection it is interesting to note that Rustban 603, a rust inhibiting oil which is believed to contain sodium petroleum sulphonate, improves corrosion resistance of a vinyl stripping lacquer as compared to a refined mineral oil containing no surface active agents such as Estic #44 oil. These results are contrary to those obtained when sodium petroleum sulphonate is added to an ethyl cellulose or nitrocellulose type stripping lacquer as in these cases sodium petroleum sulphonate has a deleterious effect on corrosion resistance.

The possibility of developing a webbing agent or lacquer having webbing characteristics equal to or better than Solution A (NOL SS-193) has been investigated. None of the polymers examined had as satisfactory properties as Solution A, but a lacquer based on a mixture of polyvinylbutyral and polyvinyl acetate has working properties which approach that of Solution A and might be considered a secondary alternate composition.

III - EXPERIMENTAL

In the experimental work on the subject problem as covered in Parlin Laboratory Report No. 900, which did not include any work with the "Vinylite" resins for reasons previously mentioned, the three most promising film forming materials of the candidates studied were ethyl cellulose, nitrocellulose and neoprene. Stripping lacquers based on these film formers in laboratory tests had such desirable properties as sprayability, strippability, durability and provided good protection from corrosion to steel test pieces when subjected to high temperature/high humidity, high temperature/salt spray and other similar tests. However, the following described

field tests on the ethyl cellulose and neoprene types, plus the results obtained from a study of the "Vinylites" indicate that the latter are for general use more promising film formers for stripping lacquers.

1. Field Tests

Field tests were run on the ethyl cellulose and neoprene types at (1) the U.S. Army Air Base, Newark, N.J., and (2) the U.S. Navy Yard, Philadelphia, Pa.

A - U.S. Army Atlantic Overseas Air Service Command
Newark Army Air Base, Newark, N.J.

In this test J-200 X-6637 and J-200 X-6639, stripping lacquers based on ethyl cellulose and neoprene, respectively, were tested as temporary protective coatings for packaging fighter planes intended for shipment overseas as deck cargo on freighters and tankers.

The ethyl cellulose lacquer, J-200 X-6637, was applied to a camouflaged P-47, Thunderbolt, by spray application with a resulting film thickness of 10-12 mils in five spray coats. Forty-one gallons of lacquer and eight gallons of thinner were required to complete the job. When tested for strippability at the end of 24 hours, the film was readily strippable and the coated plane was O.K. for shipment to the C.B.I. theatre by Colonel W.E. Nicol, Chief of Maintenance. However, the ethyl cellulose film was not as tough and rubbery as the vinyl type regularly being used at Newark for this purpose, and for this reason it was felt to be inferior to the vinyl type.

The neoprene stripping lacquer, J-200 X-6639, was applied to an unpainted P-51, Mustang, by spray application to give a film thickness of 9-10 mils in five spray coats. Twenty-five gallons of lacquer and five gallons of thinner were required to complete the job. On this plane it was decided to hold up shipment until it could be determined that the film would strip. Normally this would require a period of two weeks at a minimum temperature of 75°F. At the end of two weeks the film was strippable in some areas, but not in others. A check on the strippability two weeks later showed little improvement and it was decided to strip the film off and to package the plane in the normal manner. As later laboratory tests showed, the failure of the neoprene to fully vulcanize and acquire enough film strength to be readily strippable was due to the low temperature prevailing at that time. (See Chart IV at end of this report.) Moreover, had it been fully

vulcanized it would still have been inferior in film strength to the vinyl type then being used at Newark. It did, however, have good abrasion resistance.

B - U.S. Navy Yard, Philadelphia, Pa.

The neoprene composition was also field tested aboard the U.S.S. North Star at the U.S. Navy Yard, Philadelphia, Pa. Here it was tested as a protective coating for packaging topside equipment aboard ships laid up for storage. In this test, a range finder was packaged in the following manner:

A web, sprayed from a mixture of Solutions A and B (NOL SS-193) was used to first envelop the range finder. The neoprene solution was then applied by spray application over the web to a film thickness of 40 mils. Nine gallons of neoprene lacquer were required. The package was then opened and silica gel placed inside together with a humidity indicator and a polished 40 mm projectile. A "Vinylite" sheet (0.064 inches thick) was then sealed into the package to act as a window.

At the end of four months' exposure, at which time all the test packages were removed from the U.S.S. North Star, the neoprene package was still in good shape with no rust on the projectile and the indicator showing an inside relative humidity of less than 30%. In this application the neoprene type stripping lacquer was inferior to the NOL SS-193 type mainly in application properties, as more skill and care are required in order to get the proper degree of tautness. It also has lower tensile strength, but at the film thickness at which it was applied, this difference may not be serious.

Further field tests are underway at the Naval Air Experimental Station, U.S. Navy Yard, Philadelphia, Pa. on the ethyl cellulose, neoprene and a vinyl type stripping lacquer as temporary protective coatings for aircraft component parts during outdoor storage. These coatings were applied by spray to painted aircraft wing sections at a film build of 12-15 mils and have been on exposure at Philadelphia since December 1944. No results of these tests have been communicated to the writer of this report as of this date.

No field tests were conducted on the nitrocellulose type of strippable coating because of its well-known inflammability. However, exposure tests indicate that this type is definitely more durable than the ethyl cellulose type, equal or slightly more durable than the neoprene, and may be equally as durable as the vinyl type.

Based upon the results described above and laboratory evaluation of the "Vinylites" as described below, it is felt that for most purposes the vinyls represent the most promising of the film formers yet examined for use in sprayable, strippable, protective coatings.

In order to study the durability of the NOL SS-193 stripping lacquer and various modifications of it as well as to compare it with the neoprene type stripping lacquer, a series of miniature packages (suggested by the Naval Ordnance Laboratory at Silver Spring, Md.) have been prepared as described below and are now on exposure at Parlin.

The packages consist of one cubic foot "dog houses" which have been enveloped with a web sprayed from a mixture of Solutions A and B (NOL SS-193) over which was applied the various topcoat and topcoat systems listed below. The films were sealed to the base with Tygon TP-107A Adhesive. The package was cut open and a 40 mm polished projectile, a one pound bag of "Silica Gel" and a humidity indicator were placed inside. A thermometer was also placed in the films marked with an asterisk (*) in the table below. A rigid "Vinylite" sheet (.064 inches thick) was sealed over the 4x4" opening to serve as a window. The films were sprayed to a thickness of 30-40 mils.

The following films are being tested:

- (1) NOL SS-193*
- (2) NOL SS-193 plus 5% aluminum paste*
- (3) NOL SS-193 pigmented with carbon black*
- (4) NOL SS-193 pigmented with titanium dioxide/lampblack*
- (5) Alternating coats of NOL SS-193 pigmented black and yellow (lead chromate) with the black as the final coat.
- (6) Black (carbon) vinyl based on VYNS/VYHH (25/75) and plasticized with tricresyl phosphate.
- (7) Aluminized vinyl (5%) based on VYNS/VYHH (25/75) and plasticized with tricresyl phosphate.
- (8) Gray vinyl (titanium dioxide/lampblack) based on VYNS/VYHH (25/75) and plasticized with tricresyl phosphate.
- (9) Alternating coats of a black (carbon) and yellow (lead chromate) vinyl with black as the final coat. Both formulations based on VYNS/VYHH (25/75) and plasticized with tricresyl phosphate.
- (10) Clear modification of NOL SS-193 containing straight VYNS (J-1300-X-7147).
- (11) Composition used in (10) but pigmented with carbon black.
- (12) Clear modification of NOL SS-193 in which Estic #44 oil is used in place of Rustban 603.

- (13) Composition used in (12) but pigmented with carbon black.
- (14) Clear modification of NOL SS-193 in which Estic #44 oil is used in place of Rustban 603, and in which VMCH is used as 10% of the resin replacing VYNS.
- (15) Composition used in (14) but pigmented with carbon black.
- (16) Thirty mils of NOL SS-193 followed by 10 mils of carbon black pigmented NOL SS-193.
- (17) Black Neoprene Stripping Lacquer.
- (18) Aluminized Neoprene Stripping Lacquer.

These packages have now been on exposure for three months and all appear to be in satisfactory condition with the relative humidity in all packages being less than 30%, and none of the steel projectiles showing rust.

A recent check on the temperature variations in the packages having no pigmentation, pigmented black, gray and aluminum gave the following results:

	<u>Inside</u>	<u>Outside</u>
(1) NOL SS-193 clear	104°F	90°F
(2) NOL SS-193 pigmented black	102°F	90°F
(3) NOL SS-193 aluminized	100°F	90°F
(4) NOL SS-193 pigmented gray	103°F	90°F

Because of the apparent inconsistency in the above temperature readings it is felt that in order to get truer data on the effect of various pigments on heat absorption, it may be desirable to run field tests on packages having a larger surface area. In addition to this we are planning on running some tests to determine the temperature of stripping lacquer films pigmented gray, black and aluminum when exposed to direct sunlight.

2. General Evaluation of the Vinyl Resins

The evaluation of the vinyl chloro-acetate copolymers for use in stripping lacquers indicates that two general types are desirable: (1) one type based on the high molecular weight/high vinyl chloride content copolymers such as used in NOL SS-193 for use where wide openings are to be bridged and the film is for the most part unsupported, and hence must have maximum strength and maximum cold-crack resistance, and (2) one type based on more soluble, lower molecular weight, lower vinyl chloride content copolymers as represented by J-200 X-7012 for use where the film for the most part is to remain in contact with the surface of the equipment to be protected.

Three typical compositions are shown below:

For use where the film will be unsupported -

J-200-X-7131 (NOL SS-193 pigmented)

"Vinylite" VYNS	10.9%
"Vinylite" VYNL	2.8
dioctyl phthalate	5.5
Rustban 603	3.4 (Standard Oil of N.J.)
Stabilizer A	0.3 (B.F. Goodrich)
carbon black	2.1
methyl ethyl ketone	75.0
	<u>100.0%</u>

For use in direct contact with surface of equipment to be protected -

(a) J-200-X-7012

"Vinylite" VYNS	5.3%
"Vinylite" VYHH	15.9
tricresyl phosphate	8.5
Estic #44 oil	1.7
Stabilizer A	0.4
lampblack	3.2
methyl ethyl ketone	26.0
toluene	13.0
methyl isobutyl ketone	26.0
	<u>100.0%</u>

(b) J-200-X-7182

"Vinylite" VYNS	8.2%
"Vinylite" VYHH	8.0
"Vinylite" VMCH	0.3
dioctyl phthalate	6.6
Estic #44 oil	1.6
Stabilizer A	0.3
lampblack	2.3
methyl ethyl ketone	37.6
methyl isobutyl ketone	25.1
	<u>100.0%</u>

Formulation J-200-X-7131 is the recommended pigmented modification of NOL SS-193 and is designed to impart maximum durability. Formulations J-200-X-7012 and J-200-X-7182 are representative of the type which is applied in direct contact with the surface to be protected. The latter, J-200-X-7182, is formulated to have a better cold-crack resistance than J-200-X-7012, and to have an adhesion to Alclad of 1.5 to 2.5 pounds per inch. A sacrifice in total solids at spraying viscosity is required to obtain the improved cold crack resistance.

The following are the results of laboratory evaluation of the vinyl resins which led to the development of the above formulations:

A - Resins

Three grades of "Vinylite" resins are available from Carbide and Carbon Chemical Corporation which lend themselves for this purpose. They are:

VYNL - a copolymer of vinyl chloride and acetate having a vinyl chloride content of 93-95% and an average molecular weight of 24,000.

VYNS - a copolymer of vinyl chloride and acetate having a vinyl chloride content of 88.5-90.5% and an average molecular weight of 16,000.

VYHH - a copolymer of vinyl chloride and acetate having a vinyl chloride content of 85-88% and an average molecular weight of 10,000.

A comparison of the physical properties of three typical compositions containing them are as follows:

	2098-189-1	2098-189-2	2098-189-3	Ratio
"Vinylite" VYNL	3.1%			10.0
"Vinylite" VYNS	11.9	16.5	5.3%	
"Vinylite" VYHH			15.7	
dioctyl phthalate	6.0	6.6	8.4	4.0
Rustban 603	3.7	4.1	5.2	2.7
Stabilizer A	0.3	0.3	0.4	
methyl ethyl ketone	75.0	72.5	65.0	
	100.0%	100.0%	100.0%	
total solids	25.0%	27.5%	35.0%	
visc. (#15 DuPont cup)	24 sec.	22 sec.	21 sec.	
tensile strength	1950 psi	1865 psi	1600 psi	
elongation	400%	420%	395%	
MVTR* (50 mils)	33 grams	29 grams	29 grams	

*MVTR = grams/100 square meters/hr. 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.

From the above results it can be seen that where maximum film strength is required with maximum tautening effect (see Photograph I at end of report) the higher molecular weight resins should be used. At the same time a higher degree of chemical inertness and flexibility at low temperatures is obtained. These properties are gained, however, at the expense of solubility (total solids at spraying viscosity), solution stability and sprayability.

The relative durability of each of these resins is being studied by exposure in Florida but no significant results are as yet available.

Another of the "Vinylite" resins examined was VMCH, not as the main film former, but as a modifier to increase the adhesion.

"Vinylite" VMCH is believed to be the same as VYHS except that a small amount of maleic acid has been introduced into the polymer during the polymerization process. The effect of this resin on adhesion can be illustrated as follows when added in varying proportions to a stripping lacquer based on a 1/1 blend of VYNS/VYHH and plasticizer 10/4 with dioctyl phthalate.

<u>Composition</u>	<u>Adhesion</u>
0% VMCH	= adhesion too low to be measured with available equipment
1% VMCH on resin	= 1300 grams/inch width
2% VMCH " "	= 1385 grams/inch width
4% VMCH " "	= 1965 grams/inch width
10% VMCH " "	= 3150 grams/inch width
100% VMCH	= cannot be stripped

This effect only takes place in the absence of a surface active agent such as contained in Rustban 603, as with this oil present even with straight VMCH in the ratio of 10 parts resin to one of oil, the adhesion drops to 450 grams/inch width.

Preliminary results indicate that the use of VMCH in quantities up to 10% of the resin does not have a deleterious effect on corrosion resistance or moisture vapor transmission rate and that it may even have a beneficial effect. Its effect on ultimate durability is being studied.

B. Plasticizers

A number of plasticizers are being evaluated for use with the vinyl resins, among which are:

1. dioctyl phthalate
2. tricresyl phosphate
3. Paraplex G-25
4. dibutyl sebacate
5. dioctyl sebacate
6. methoxyglycol acetate ricinoleate

The best all-around plasticizer appears to be dioctyl phthalate, although we do not have the durability experience with it that we have with tricresyl phosphate. Dioctyl phthalate gives the best combination of flexibility over a wide range of temperatures, pliability, and low moisture vapor transmission rate. Tricresyl phosphate is inferior to dioctyl phthalate mainly in flexibility at low temperatures. Dibutyl sebacate while returning better low temperature flexibility than dioctyl phthalate slightly impairs the MVTR and is inclined to be slightly more volatile. Paraplex G-25 and methoxyglycol acetylricinoleate have poorer low temperature flexibility than dioctyl phthalate and there are indications that the methoxyglycol acetylricinoleate returns poorer durability. Dioctyl sebacate, contrary to the manufacturer's (Resinous Products) claims, did not return as good cold-crack resistance in our tests as did dioctyl phthalate when used in vinyl stripping lacquer formulations.

C - Oils

Two types of oils have been evaluated for use in vinyl stripping lacquers; viz., Rustban 603 and Estic #44 oil.

Both oils have a place in the formulations depending upon the use to which the coating is to be put.

Rustban 603 while having the advantage of promoting corrosion resistance, returns a slightly higher MVTR and in uses where the film is to be adhered to the metal with an adhesive, it impairs the heat resistance of the bond (see discussion under "Adhesives" in latter part of this report). It also cannot be used when a definite degree of "controlled adhesion" is to be incorporated in the film. Such an application is as a protective coating for use in direct contact to equipment intended for outdoor storage or shipment. Here, if the adhesion is too low, there is danger of the film being stripped from the equipment by the wind if the film is accidentally ruptured.

D - Stabilizers

An evaluation of a number of stabilizers, both organic and inorganic is underway to determine their stabilizing effect against heat and light with the view of improving the durability of the vinyl stripping lacquers. Among those being evaluated are:

Organic

- Stabilizer A (the monoester of a vegetable source fatty acid manufactured by R. F. Goodrich Co.)
- Salol (phenyl salicylate)

Inorganic

blue lead

red lead

litharge

lead chromate

lead titanate

antimony oxide

Both Stabilizer A and Salol appear to have a slight stabilizing effect especially in clear lacquers. There are indications that on outdoor exposure Salol may be slightly superior to Stabilizer A, but the improvement obtained with both is very small compared to the effect of such pigments as carbon black. In addition both improve the corrosion resistance. This beneficial effect is definitely noticeable in vinyl lacquers containing Estic #44 oil and is not so noticeable in formulations containing Rustban 603. In this respect Stabilizer A is slightly more beneficial than Salol.

Exposure tests in Florida have also not gone far enough to draw any conclusions regarding the effect of the inorganic type stabilizers on ultimate durability. There are some indications that the lead pigments may have a deleterious effect on corrosion resistance. This point, however, is being checked.

E - Pigments

Several pigments and pigment combinations are now undergoing evaluation to determine their effect on the durability of vinyl type stripping lacquers. These are carbon blacks, lampblack, titanium dioxide/lampblack, lead chromate, cadmium sulphide and aluminum, with and without stabilizers.

Although the exposure series have not progressed to the point where definite conclusions can be drawn, the evidence obtained so far indicates that pigmentation definitely improves the durability of a vinyl type stripping lacquer and that carbon black pigmentation offers the best possibilities of giving a film its maximum durable life.

Photograph III at the end of this report shows the beneficial effects to be gained by pigmenting a clear vinyl stripping lacquer. The panels shown in this photograph were coated to a 10 mil film thickness with a vinyl stripping lacquer composed of "Vinylite" VYHH - 10.0/tricresyl phosphate - 3.0/Estic #44 oil - 1.0. The panel on the right was pigmented with carbon black/red lead, the one on the left with titanium dioxide/lampblack/red lead, while the one in the center is unpigmented. All were exposed nine months in Florida at a 45° angle facing south. The two pigmented modifications

are still readily strippable, have retained a fair degree of flexibility and have protected the steel substrate from corrosion. The clear, however, has become dark and very brittle and has flaked off the panel which is badly corroded. This deterioration of the film was apparent at the end of one month's exposure at which time the clear film showed surface checking, had darkened, and the steel substrate began to show signs of rusting.

Photograph II shows four microphotographs of films of clear and pigmented NOL SS-193 stripping lacquers which have been exposed three months in Florida as unsupported films on wooden frames. These films were sprayed over the web coat to a film thickness of approximately 40 mils. The clear film is the only one showing signs of deterioration, evidenced by small surface checking and darkening. Photograph (a) is the clear before exposure while (b) is after three months' exposure. Photographs (c) and (d) represent the clear pigmented with carbon black, and the clear with a 5 mil thick topcoat of a black pigmented vinyl stripping lacquer. Neither show any signs of deterioration. (The difference in smoothness which is noticeable between photographs (c) and (d) is due to differences in spray application and existed before the films were exposed.) This would indicate that perhaps only a topcoat of 5-10 mils of a black pigmented vinyl stripping lacquer is all that is necessary to give the desired degree of outdoor durability.

Vinyl stripping lacquers pigmented with titanium dioxide/lampblack and with lead chromate also give evidence that added durability can be imparted to a clear with these pigments, but it is not expected that they will return as good durability as can be obtained with carbon black. Modifications of the clear pigmented with cadmium sulphide were better than the clear for durability also but show signs of beginning to fail at the end of four months' exposure in Florida.

The use of aluminum flake is not being recommended at this time as there is some evidence that it weakens the corrosion resistance of the film. It does, however, tend to decrease the MVTR but the amount of aluminum needed to obtain an appreciable decrease in permeability also tends to reduce the toughness of the film by decreasing its tensile strength and elongation. However, it may be that a final topcoat of an aluminized vinyl lacquer over the clear may be desirable, particularly because of its ability to reflect rather than absorb heat and light. It is recommended that field tests be

made on large pieces of equipment to check the difference in the heat absorbed in the package when topcoated with black, gray and aluminum vinyl lacquers.

F. Solvents

The following work with solvents has been done on the vinyl stripping lacquers both for the NOL SS-193 type and the J-200 X-7012 type.

In the NOL SS-193 type straight methyl ethyl ketone can be used with satisfactory results for most conditions of application. However, when the lacquer is to be sprayed under conditions of high temperature/high humidity, the use of small amounts of methyl isobutyl ketone is recommended. Several batches of NOL SS-193 have been formulated with other solvent compositions and their effect on speed of solution, sprayability, properties of the sprayed film, and stability of the solutions have been noted.

All except No. 5 blend shown below appeared to be promising in the event sufficient methyl ethyl ketone is not obtainable. Listed below each blend is the viscosity of the NOL SS-193 solution obtained initially and after aging.

	1	2	3	4	5	6	7**	8**
MEK	100	90	80	70	60	50	40	30
MIBK	0	0	0	0	0	10	5	10
toluene	0	10	20	30	40	20	29	27
acetone	0	0	0	0	0	20	66	63
original visc.*	17"	20"	20"	24"	25"	19"	20"	20"
after 5 days	19	21	22	27	35	24	20	21
after 1 month	19	21	23	26	34	26	21	21

*viscosity determined at 25°C. in duPont #15 cup

**suggested by Lt. Wm. H. Holst.

It would, therefore, appear that if necessary the amount of methyl ethyl ketone needed can be materially decreased or entirely eliminated.

In the J-200 X-7012 formulation the solvent combination used is considerably slower than in the NOL SS-193 type. This is necessary because J-200 X-7012 is applied at a considerably less film thickness (10-15 mils) and for this reason must have a lesser degree of porosity. The solvent combinations recommended for this type are:

	(1)	(2)
methyl ethyl ketone	40	60
toluene	20	"
methyl isobutyl ketone	40	40

No.2 blend is recommended for use where a high percentage of VYNS is used such as in J-200-X-7182.

G - Application

In the spray application of the NOL SS-193 nothing can be added here which is not already covered in Manual OP-11485 (Preliminary). However, for the J-200-X-7012 and J-200-X-7182 the following recommendations are made. Spraying should be done either at package viscosity or reduced slightly with a 1/1 mixture of toluene and methyl isobutyl ketone. Although other types of spray equipment can undoubtedly be used, it is recommended that a De Vilbiss MBC gun equipped with a #70 or #76 cap and an E tip be used. Pressure at the gun should be 75 pounds or greater and 20-35 pounds on the fluid. Under these conditions a non-porous 10 mil thick film can be laid down in 3-4 spray coats. A minimum elapsed time of five minutes between coats is desirable.

3. Adhesives

One of the main problems in developing the NOL SS-193 system of packaging has been the development of a satisfactory adhesive for adhering the film to the base of equipment to be packaged.

A survey was made of potential candidates for this job which would give a better bond than Tygon TP-107A, the adhesive originally recommended. It was found that adhesives such as "Gaytex" or "Pliobond" which are based on a phenol-formaldehyde resin modified butadiene/acrylonitrile copolymer give the best initial bond and least thermoplasticity of any of the adhesives tested. Some of these adhesives were:

- (1) Tygon TP-107A
- (2) "Vinylite" VMCH
- (3) "Vinylite" VMCH plasticized with Paraplex G-25
- (4) "Vinylite" VMCH plasticized with methoxyglycol acetylricinoleate
- (5) 4653, a self-curing "Butacite" type
- (6) Gaytex
- (7) Pliobond
- (8) C-62-53, a duPont experimental cement similar to Gaytex

Of these, Nos. 6, 7 and 8 were best in initial properties.

In addition, it was also found that initial bond strengths and resistance to loosening of the bond under a load at elevated temperatures can be improved by (1) using Estic #44 oil in place of Rustban 603 and (2) replacing 10% of the resin in NOL SS-193 with VMCH resin.

The following table gives the strength required to pull a one inch strip of (1) NOL SS-193, (2) Estic #44 oil modification of NOL SS-193 (2098-179-1) and (3) Estic #44 oil modification with 10% of resin replaced by VMCH (2098-171-1) from steel coated with the following adhesives: (The adhesives were brushed on 4x12" steel panels which had been sanded to a smooth surface and allowed to dry one hour. The strippable coatings were then sprayed over the adhesive to a film thickness of 30 mils and the system then allowed to age at room temperature (75°F. $\pm$ 5°) for one week before tests were made.)

	<u>Adhesion in Grams</u>
NOL SS-193 over Pliobond	1385
Gaytex	1350
C-62-53	425
VMCH	too low to be measured
VMCH/Paraplex G-25	too low to be measured
2098-179-1 over Pliobond	1670
Gaytex	1735
C-62-53	1015
VMCH	540
VMCH/Paraplex G-25	955
2098-171-1 over Pliobond	1675
Gaytex	1900
C-62-53	1135
VMCH	800
VMCH/Paraplex G-25	2250

However, thermoplasticity tests made at a 180° pull with a dead load of 1/2 pound per inch width indicate that Pliobond and Gaytex have the best heat resistance and this is especially true under the 2098-179-1 and 2098-171-1 modifications of NOL SS-193.

Check tests on NOL SS-193 and 2098-179-1 over Gaytex and Pliobond made at a 45° pull which more closely simulate the most severe conditions to be met in service gave the following results. In the following tables 9-1/2 inches is the maximum distance the film can be stripped.

	180°F.	260°F.	340°F.
NOL SS-193 over Pliobond	9.5 in. in 45 min.	9.5 in. in 75 min.	9.5 in. in 48 hrs.
Gaytex	9.5 in. in 1 hr.	9.5 in. in 5 hrs.	9.5 in. in 48 hrs.
2098-179-1 over Pliobond	1.5 in. in 2 hrs.	9.5 in. in 30 hrs.	6.2 in. in 48 hrs.
Gaytex	0.1 in. in 2 hrs.	0.2 in. in 30 hrs.	0.8 in. in 48 hrs.

These tests indicate that the use of Rustban 603 in formulation NOL SS-193 does not give the heat resistant bonds with "Gaytex or Pliobond" as are obtained with Estic #44 oil, and that Pliobond is inferior to Gaytex. However, because these tests may be considerably more severe than will be encountered in actual service and because these results have not been correlated with those obtained in the field, the apparent weakness of these adhesives in resistance to a dead load pull at elevated temperatures, may not be as serious as it would appear from the tests. As for the differences encountered between Gaytex and Pliobond which are supposedly identical in composition, batch to batch variation of the adhesive may be the answer. By changing the oil in NOL SS-193 from Rustban 603 to Estic #44, an improvement in heat resistance of the bonds can undoubtedly be obtained but this must be balanced against a slight decrease in corrosion resistance.

The systems listed in the above table are now being exposed outdoors with a dead load of 1/2 pound per inch at a 45° pull in order to determine their resistance to flow under constant load at summer temperatures.

Some preliminary experiments to develop a self-curing adhesive in order to improve the heat resistance of the bonds have not met with any success as yet. These adhesives were based on Vinylite/Hycar combinations and were two package compositions with one of the solutions containing the vulcanization agent and the other containing an ultra accelerator such as a butyraldehyde/monobutylamine condensation product.

4. Webbing Agents or Lacquers

A high-spot investigation has been made to evaluate the merits of other film formers as webbing agents or webbing lacquers having working properties equal to or better than Solution A (NOL SS-193), the webbing agent developed at the Naval Ordnance Laboratory, Silver Spring, Md. for use in conjunction with Solution B (NOL SS-193).

Among the candidates examined were:

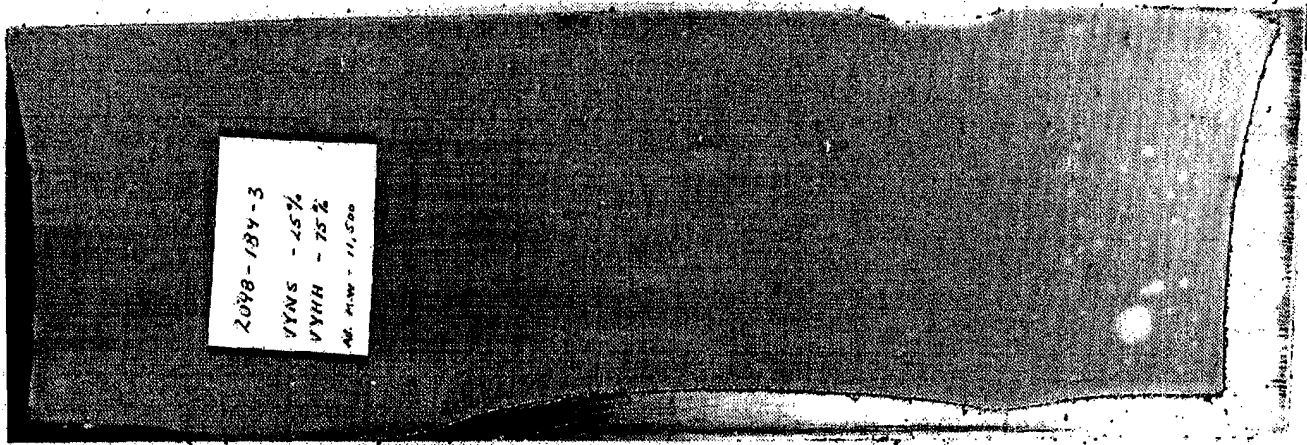
polyvinyl butyral	polystyrene
polyvinyl acetate	n-butyl isobutyl methacrylate
polyvinyl pyridine	methyl methacrylate
Styraloy (Dow Chemical Co.)	

None of the above polymers produced a lacquer with as satisfactory webbing properties as Solution A. However, a lacquer based on a mixture of polyvinyl butyral and polyvinyl acetate had webbing characteristics which approach that of Solution A, and might be considered a secondary alternate composition. This lacquer has the following composition:

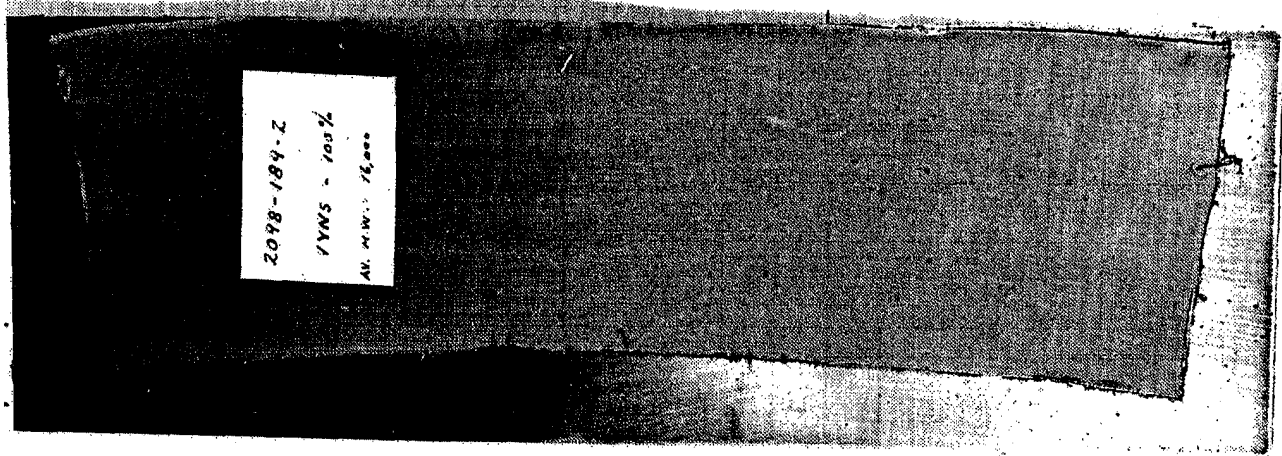
2098-282-2

polyvinyl butyral	9.5%
polyvinyl acetate	4.7
Rustban 603	2.8
ethyl alcohol	37.7
acetone	16.0
toluene	10.4
aliphatic hydrocarbon (65-105°C.)	18.9
	<u>100.0%</u>

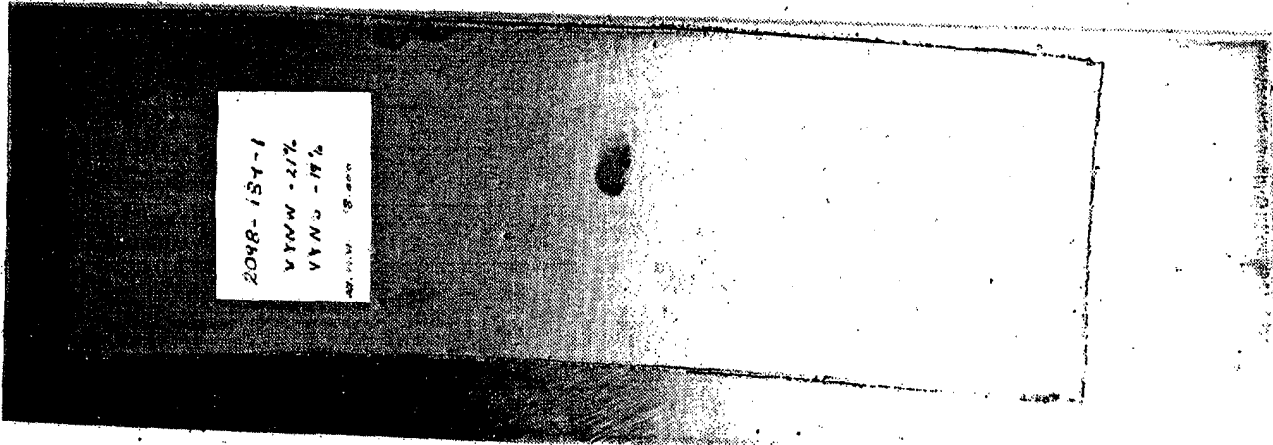
CGM:RMW
6/30/45



2048-184-3
VYNS - 45%
VYHH - 75%
AV. MW - 11,500

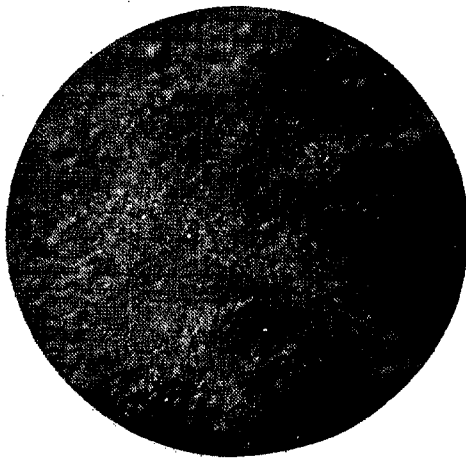


2048-184-2
VYNS - 100%
AV. MW - 16,000

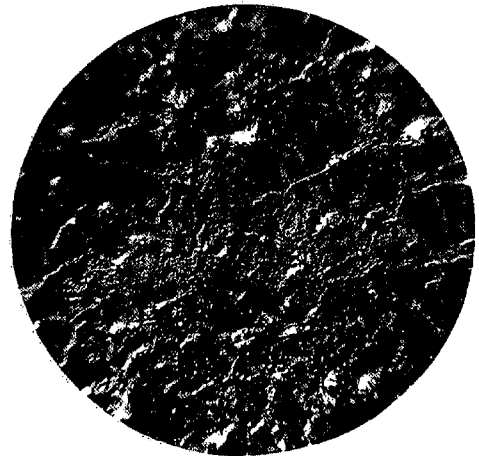


2048-184-1
VYMW - 21%
VYNS - 14%
AV. MW - 8,000

I



(a)



(b)

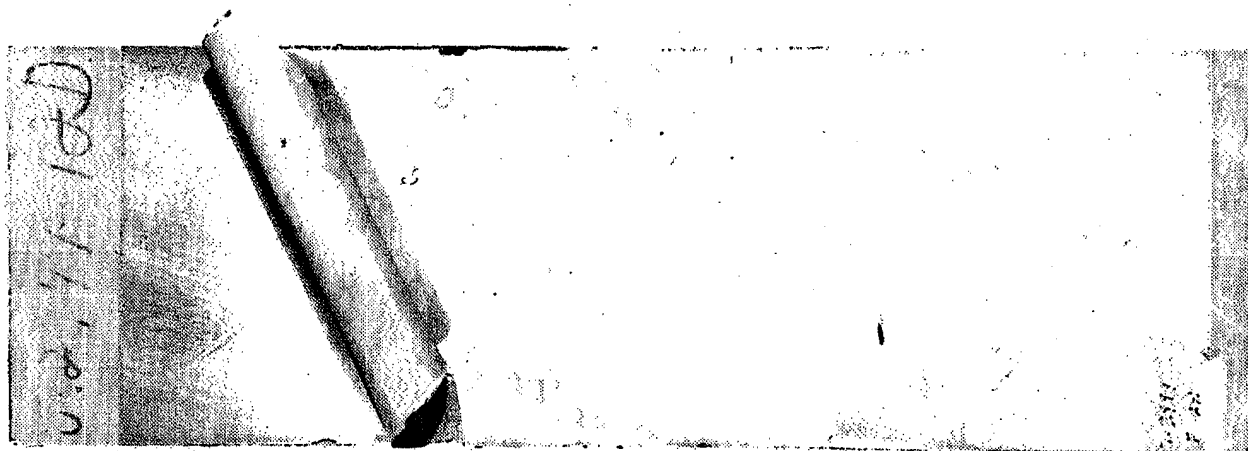
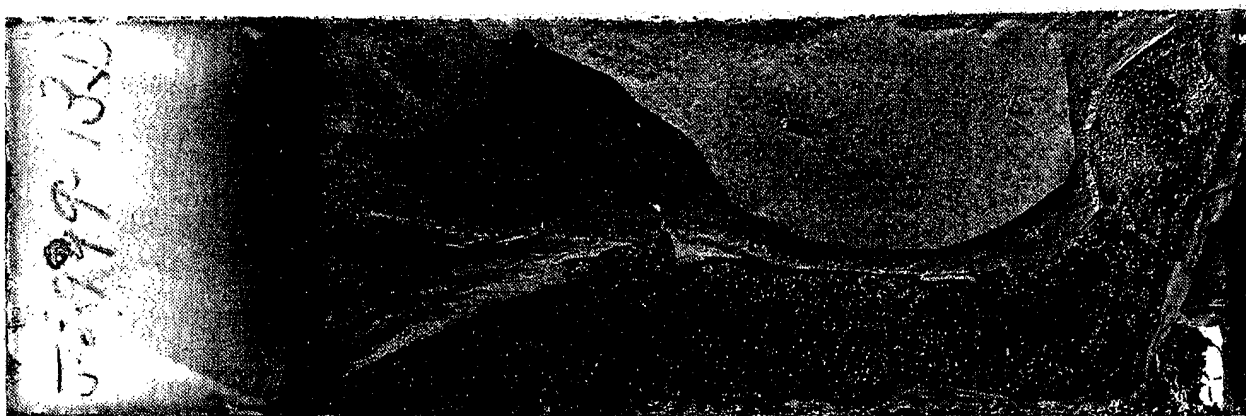
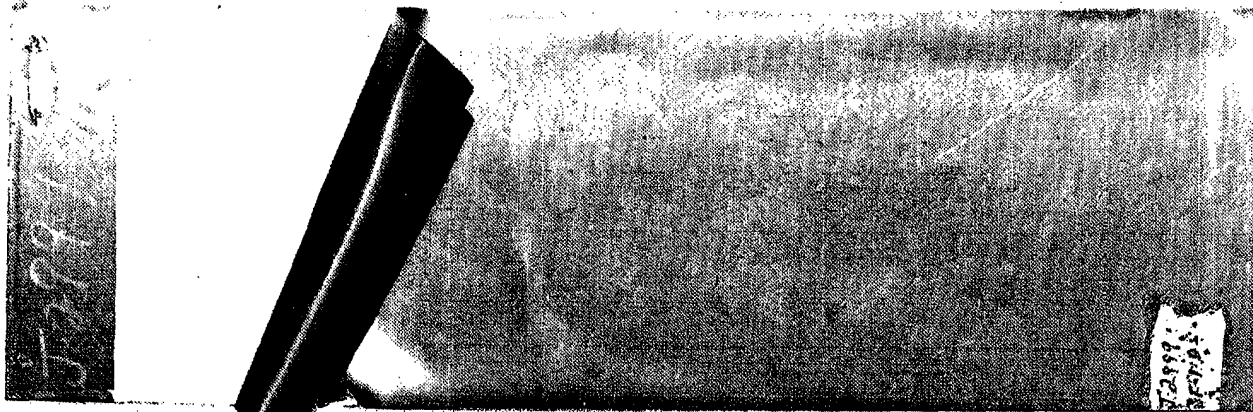


(c)



(d)

II



III

EFFECT OF TEMPERATURE
ON THE VULCANIZATION OF NEOPRENE
STRIPPING LACQUERS

