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DEVELOPMENT OF COATINGS ADHERENT TO METALS UNDER VIBRATION CONDITIONS

FINAL REPORT

May 20, 1966

BUREAU OF SHIPS, DEPARTMENT OF THE NAVY,  
CONTRACT No. N0bs 90357  
(N.Y.U. Engineering Project No. 1130)

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May 20, 1966

Max Kronstein  
Project Director

Bureau of Ships  
Department of the Navy  
Contract No. N0bs 90357

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The work reported herein has been performed in Research Building No. 3 of the Research Division, School of Engineering and Science, New York University under the direction of Dr. Max Kronstein, Senior Research Scientist. The members of the research staff who have participated in the work are:

Mr. Raymond N. Handwerker	Research Assistant
Mr. Lynne R. Harris	Research Assistant
Miss Jane B. Lian	Research Assistant
Mr. John M. Pascone	Research Assistant
Miss Andrea M. Valentine	Research Assistant
Mr. Arnold L. Van Aken	Research Assistant
Dr. William H. Napfer	Chemical Engineer
Mrs. Marion W. Kronstein	Assistant Research Scientist.

- - -

## SUMMARY

The factors which influence the life of paint systems on steel under saltwater and ultrasonic vibration have been studied. The sonic effects have been found to differ in their effect which decreases the adherence of the coating system and their effect which influences the coherence of the coatings with resultant cavitation. It has been studied in what form the transducer energy is distributed through saltwater: some forms of transducers give up the energy in a form where it is being dispersed throughout the whole saltwater area, with the greatest energy appearing close to the entry area of the energy; but the energy continues to be effective in widening areas at greater distances from the entry, and the energy is being reflected from the metal walls of the saltwater tank and from the upper limit of the saltwater/air interface back into the water. Another transducer gives off powerful energy but only at a very short distance from the source and according to the narrowing diameter of the energy source area. Large ship transducers can have both effects, representing a bundle of high-energy centers with the additional spreading of energy outside of the area directly facing the transducer head. ( PART I)

The forms of failure which take place are: loosening of parts of the film from the steel substrate, local pinhole formation, and filament formation. (PART II)

Increased adherence has been found to result from: (a) step-by-step surface preparation, which includes surface inhibition and the driving off of entrapped air in the valleys of the surface profile; (b) the use of primers, including the specification wash-primer (F 117) and a red lead or zinc chromate vinyl primer so applied that there is inter-reaction between one application and the next; (c) avoiding solvent retention in each application before subsequent coatings are applied; (d) bringing the paint system to a desirable state of cross-linking, or polymer state, without going so far as to lose coherence in the paint film. (PART III)

A description of the pre-treatments used and experimental coating systems developed is given and discussed. (PART IV)

## BACKGROUND: THE PROBLEM.

The project was concerned with the observation which had been made in Navy practice that under the influence of supersonic radiation and in the area of radar radiation ship coatings develop areas of failure. At the start of this project it had been assumed that these failures were caused primarily by a loss of adhesion of the paint system under the effect of the vibration which is caused by the path of supersonic energy through the seawater and affecting the painted surfaces. The earlier period of the work on this project confirmed that under such vibration the conventional coatings and coating applications begin to develop two kinds of failure rapidly: (a) they begin to lose adhesion, especially from the edges; and (b) they develop pitting and filament areas on many parts of the surface.

Primary aims of the project as outlined at its conception were an elimination of the various sources of decreasing adhesion, and developing coating systems which would resist the vibration energy in the saltwater due to their uniformly cured condition. Both of these aims have been studied to a great extent; and the time of resistance of applied coating systems under comparative tests has increased from between 48 hours and 72 hours to several hundred hours, with panels still in good state after the extended time of exposure. The step-by-step development of the work is outlined in this report.

Nevertheless, on the other hand, it has been established that the factor of vibration is not the only characteristic of sonar and supersonic radiation: when the source of the energy is so constructed that the emitted energy is not spread out in an extended water volume but is concentrated in powerful beams of radiation, these beams cause besides vibration a strong impulse into the coating system. Such beams actually penetrate into the paint system, resulting in a piercing of the film and the formation of cavitations. This form of coating

failure is independent of the vibration factor. With the highly adherent and highly cross-linked system which offers the highest degree of adhesion, the cohesion can be lower than that required to resist the direct frontal attack of the high powered and concentrated beam.

This new problem of connecting the developed adherent and highly cross-linked system with additional elements to increase its coherence, is not yet fully solved. . The new system, whose development has come under way and which is further to be completed, must maintain the good adhesion under supersonic vibration obtained under the present contract and at the same time maintain a maximum of cohesion against a frontal attack of strong and concentrated beams of sonic and ultrasonic energy.

The present report covers the work from 27 April 1965 through 27 April 1966. The preceding work to 27 April 1965 was reported in the Intermediate Progress Report submitted May 29, 1965.

## RESULTS.

### INTRODUCTION

The work covered in this report is divided into the following sections:

I. The study of the distribution of the transducer energy under saltwater, using different forms of transducers and different energy exposures.

II. The study of the different forms of loss of adhesion which have been observed.

III. Studies on increasing the adhesion

1) by surface preparation

2) by increased inter-reaction between the surface of the metal and the first coat.

3) by a systematic build-up of the coating system, avoiding retention of solvent residues in the coating material which would interfere with the uniform curing of the system and its inter-coating uniformity. The aim is here a solid cure of the completed system.

4) by systematic increase of the degree of cross-linking in the coatings during the curing. The optimum with respect to cross-linking requires maintaining strong enough coherence to resist cavitation effects of supersonic energy when facing the transducer source.

5) by aiming for an additional development of an anti-fouling paint which will adhere to a well cured coating system and will also have enough coherence to resist the cavitation effects of the supersonic radiation when facing the transducer area.

IV. Review of the pre-treatments and coatings used

1) in the pre-treatment and priming of the metal

2) in the top coats, using specification paints and new experimental paints

3) in new forms of cross-linking throughout the paint system.

V. Review of the present status of the development.

- - -

PART I. STUDY OF THE DISTRIBUTION OF THE TRANSDUCER ENERGY UNDER SALTWATER.

The transducer energy distribution depends on the power used and on the form in which the energy is being released. The energy can either (a) be released so that it will be dispersed over an extended area, as when a transducer is mounted under the center of the bottom of a degreasing tank; or (b) in another form a strong transducer might have a head of limited diameter and the head itself might be so constructed that the emitted energy is not spread out in a saltwater tank but is concentrated in a small area in front of the head. In form (a) the energy will enter the center area of the bottom of the tank and disperse throughout the tank under conditions which have been well established during the work. Coated panels in such a tank will be exposed to energy attack as well as to the vibration effect caused by this energy. In form (b) the energy will cause a cavitation effect on an exposed surface, with the diameter of the cavity smaller than the diameter of the head of the transducer. Due to this pattern the center of the energy attack will be quite close to the head and will decrease with the distance. It will not cause any special vibration effect to such an extent as to cause a general loss of adhesion.

If a large transducer is used such as is used in certain Naval Laboratories the source might release bundles of energy, most of which is centered in a number of beams, with a minor extent of energy radiating to the sides of these beams. Such systems will cause a number of high powered effects which result in a cavitation formation for each of the beam centers. Some of the radiation spreads out from this bundle of center beams over a wider area in the water. Therefore, both the factors of type (a) as well as the factors of type (b) will be of importance.

This is being discussed as follows:

(a) Using a tank where the transducer is mounted under the center of the bottom of the tank:

In the Intermediate Progress Report covering the work from 27 April 1964 to 27 April 1965, the test panels were exposed in 5% saltwater solution in the test tank of the SONOGEN LGTH-40 supersonic test device. No methods had been available to determine at that time the manner of distribution of the energy throughout the test tank. In the meantime such a method has been developed by this group.

Data about the instrument are given in TABLE 1.

The spreading of the energy from the area of entry at the bottom of the tank was first measured in its effect on aluminum foil and on coated steel panels as the vertical spreading upwards from the zone of entry. ( See TABLE 2) This was done using the fact that an 0.5 mil thick aluminum foil is progressively deteriorated by the entering energy to which the foil is exposed in 5% saltwater.

The size of the tank was as follows:

Length	5 inches
Width	5 inches
Height of water level	6 inches.

In TABLE 3 the horizontal spreading of the energy was measured by exposing in horizontal position first one foil at a distance of 0.5 cm above the entry area, a second one afterwards at a distance of 2.5 inches above the area of entry, and finally a third one afterwards at a distance of 5 inches above the area of entry.

Since TABLE 2 had shown that the energy decreases with the height above the area of entry, the length of exposure was increased also with the increasing distance. The results of the table show that with the increase of distance the intensity of the waves decreases; but on the other hand the diameter of the area of wave effect increases. This was shown in FIGURE 4 B of Letter Report No. 20: when the foil was exposed horizontally 1 cm above the entry area, the diameter of the pinhole and cavitation area was 6.5 cm. or about half the diameter of the tank

\* 6.5 cm = 2.559 in.

TABLE 1.

SOME DATA ON THE SONOGEN LGTH-40 SUPERSONIC TEST DEVICE

Manufactured by Branson Instruments, Inc., Stamford, Conn, as MODEL LGTH-40  
SONOGEN ULTRASONIC GENERATOR WITH A TANK .

Generator: Power output: average 40 watts with 80 watts peak on pulses.

Frequency: 25 kc

Input: 115 VAC/ 50-60 cycle and 120 watts.

Transducer: Frequency: 25 kc

Maximum Operating Temperature: 200° Fahrenheit.

Heater capacity: 125 watts.

The transducer was mounted underneath the bottom of the tank.

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TABLE 2.

VERTICAL SPREADING OF ENERGY

TESTED BY SUSPENDING AN ALUMINUM FOIL ( 0.5 mil THICK) VERTICALLY OVER  
THE AREA OF ENTRY OF SUPERSONIC VIBRATION.

DISINTEGRATION OF THE FOIL DUE TO THE ENTERING ENERGY:

TIME	HEIGHT OF DISINTEGRATION	COMMENT
1st Period		
1 min.	2.5 cm. above the entry area.	Rate of spreading in the 1st Period: 2.5 cm./min.
2nd Period		
1 min. plus 1.5 min.	2.5 cm plus 2.5 cm above entry area( with a pattern of additional blisters indicating the continuing spreading of the disintegration.)	Rate of spreading in 2nd Period: 1.66 cm./min., or due to increasing distance 1/3 less than in 1st Period.
3rd Period		
1 min. plus 1.5 min. plus 0.5 min.	2.5 cm. plus 2.5 cm. plus 1.0cm.	Full disintegration with additional 2 cm. of partial disintegration.

- - -

TABLE 3.

SPREADING OF ENERGY FROM THE AREA OF ENTRY

TEST DEVICE USED: SONOGEN LGTH-40 SUPERSONIC TEST SET-UP.

ONE ALUMINUM FOIL ( 0.5 mil thick) WAS SUSPENDED IN HORIZONTAL POSITION COVERING THE WHOLE TANK AREA ABOVE THE BOTTOM, WITH ITS ENTRY AREA OF SUPERSONIC ENERGY.

A) DISTANCE FROM ENTRY AREA: 1 cm.

TIME OF EXPOSURE	EFFECT OF FOIL	DIAMETER OF CAVITIES-AREA	DIAMETER OF SINGLE CAVITIES
30 sec.	CONSIDERABLE FORMATION OF CAVITIES AND AREA OF SMALL BLISTERS.	6.5 cm(2.559 in)	0.5 to 1 cm.
60 sec.	SIZE AND DENSITY OF CAVITIES INCREASED.	6.5 cm	0.5 to 1.5 cm.

B) DISTANCE FROM ENTRY AREA: 2.5 INCHES (6.3 cm)

30 sec. VERY MANY SMALL BLISTERS 9 cm.

60 sec. INCREASED BLISTERING.

3 min. IN CENTER AREA ONLY SMALL PITS BUT LARGER CAVITIES ABOUT 3.5 cm FROM CENTER. 9 cm. 0.5 to 1 cm.

( Note that here the cavity formation required about 5 times the time of exposure, while the distance has been increased only 2.5 times. The diameter of the cavitation area had increased from 6.5 cm. to 9 cm., or by 38%.)

C) DISTANCE FROM ENTRY AREA: 5 INCHES ( 12.6 cm).

4 min. REQUIRED FOR SEVERE CAVITIES 12 cm 0.5 to 1 cm.  
SMALL PITS IN THE CENTER AREA; LARGER CAVITIES IN THE OUTER RANGE OF THE 12 cm. DIAMETER AFFECTED AREA.

( Time required for formation of the larger cavities increased by 33%, when the distance between TEST B AND C doubled. Nearly the whole tank area is now affected by the energy.)

( See Photos to B) and C) in Letter Report 20, FIGS 3B , 3C and 4A).

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bottom. When the foil was exposed 2.5 inches (6.3 cm) above the bottom of the tank the diameter of the affected area was 9 cm ( 3.543 in.) or about 70% of the tank area. When the foil was exposed 5 inches (12.6 cm ) above the bottom , the diameter of the affected area was 12 cm ( 4.724 in.) , or more than 90% of the tank area.

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This gives the pattern of the energy spreading in the test tank.

Upon extending the exposure tests to paint coated SAE 1010 steel panels, it is to be considered that the energy can only penetrate the paint film but not the steel, and that therefore different effects will be visible on the painted side which is facing the entry area and on the reverse side of the panel, where the energy is passing through the panel into the inside of the paint. This is the case especially when the panels are exposed close to the entry area of the energy. The data observed on coated panels are shown in TABLE 4. In the test of this Table the distances are different from the tests with foils, in order to take account of the panel thickness, and in order to allow that the panels are in all distances fully immersed in the saltwater.

The first test was made with the lower panel side 0.5 cm. from the entry area of the vibration. In the second test, the same 2.5 inches ( 6.3 cm) distance was used as with foils. In the third test, the panel was exposed 4.5 inches (12.6 cm) from the bottom, in order to immerse the reverse side also.

The test panels used in this specific study were either coated, after wire-brushing, with one coat washprimer MIL-P-15328 (F.117) and two coats red lead vinyl primer MIL-P-15929 B (F. 119); or the two coats of red lead vinyl primer were applied directly to the wire-brushed steel.

In TABLE 4 the interesting observation is made that the energy waves which are deflected by the metal surface and are moving toward the walls of the tank are reflected from there back into the tank. Therefore they do affect the edges of

TABLE 4.

EXPOSING PAINT COATED 1010 STEEL PANELS UNDER CORRESPONDING CONDITIONS TO THE HORIZONTAL EXPOSURE TESTS OF TABLE 3.

PAINT COATING: 4 mils on each side of panel.

SIZE OF PANELS: COVER MOST OF TANK AREA, WITHOUT TOUCHING THE WALLS.

I. TEST GROUP EXPOSED WITH PANEL 0.5 cm ABOVE ENTRY AREA OF ULTRASONIC VIBRATION.

PANEL WITHOUT WASHPRIMER: AFTER 2 HOURS EXPOSURE, EVIDENT LOSS OF ADHESION DUE TO VIBRATION. PITTING EFFECT ON SIDE FACING THE SOURCE AS WELL AS ON REVERSE SIDE.

PANEL WITH WASHPRIMER: SIDE FACING THE SOURCE: PATTERN OF LOCAL FAILURES OVER AN AREA OF TWO SQUARE INCHES. ON REVERSE SIDE, AREA OF LOCAL FAILURE OVER ONE SQUARE INCH AREA.

II. TEST GROUP EXPOSED WITH PANEL 2.5 INCHES ( 6.3 cm) ABOVE ENTRY AREA.

THE PANELS WERE EXPOSED FOR 9 3/4 hours.

WITHOUT WASHPRIMER: THE SIDE FACING THE ENTRY AREA SHOWS A FAILURE AREA NOT AT THE CENTER OF THE PANEL BUT BETWEEN THE CENTER AND AN EDGE AREA. ( THIS CORRESPONDS TO THE PATTERN OF THE SPREADING OF ENERGY IN TABLE 3).

WITH WASHPRIMER, AND THEREFORE GREATER ADHESION: LESS FAILURE BUT IN THE SAME AREA. THE REVERSE SIDE SHOWED HARDLY ANY EFFECT.

III. TEST GROUP EXPOSED WITH PANEL 4.5 INCHES (12.6 cm) ABOVE ENTRY AREA.

THE PANELS WERE EXPOSED FOR 17 1/2 HOURS.

THE SIDE FACING THE ENTRY AREA SHOWS, WITHOUT WASH-PRIMER AND WITH WASH-PRIMER, LITTLE EFFECT. THE EDGES ARE EXPOSED TO THE ENERGY PRESSING BETWEEN THE PANEL EDGES AND THE TANK WALL, AND SOME LOSS OF ADHERENCE APPEARS IN THIS AREA.

THE SIDE FACING THE UPPER LEVEL OF THE SALTWATER AND EXPOSED TO THE ENERGY WAVES REFLECTED FROM THE UPPER LEVEL OF THE WATER, SHOWS MORE FAILURE AREAS AND AREAS CONSIDERABLY SPREAD OUT OVER THE PANELS.

- - -

the coated panel and lift the paint film from there off the steel. This is the case especially in the area 4.5 to 5 inches from the entry area, where the tests of TABLE 3 have shown that here the energy waves are affecting more than 90% of the tank area, even before the reflection effect.

When the energy waves reach the upper level of the saltwater in the tank, they are reflected back from there into the tank, so that in the case of the upper position of the panels the painted side facing the entry area shows hardly any pitting at a time when the side facing the reflection area of the water surface shows considerable areas of failure. ( These tests are described in more detail in Letter Report No. 23.)

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(b) Using a different type of transducer: the SONIFIER, MODEL S-125.

The pass of the transducer energy depends not only on the power and frequency of the generator, but also on the form in which the transducer gives off its energy. For testing the influence of this characteristic, a highly concentrated energy test-head was used in the form of the SONIFIER, MODEL S-125 (Heat Systems Company, Melville, Long Island, New York). This instrument is 15 inches long and has a test-head one-half inch in diameter, so that the energy is given off a base of this diameter. The instrument has the shape of an electric drill.

To study its effect on aluminum foils as well as on painted panels, a new test set-up was built. It was a wooden, water-tight tank, 12 inches high, 12 inches wide and 15 inches long filled with 5% saltwater. Seven and one-half inches from one end a movable frame was inserted for attaching the test panel. To allow free movement of the energy waves, this frame had a rectangular window  $3\frac{1}{2}$  inches by 7 inches in size, located in front of the instrument head. The transducer passes first a water-free chamber and enters into the saltwater tank. The head is mounted 0.5 cm (0.1968 inch) from the test panel. The manufacturer claims that the instrument gives off 1000 watts/sq. inch, or 500 watts from the one-half sq. inch head within a most effective distance of  $\frac{1}{4}$  to  $\frac{1}{2}$  inch.

When the aluminum foil is mounted 0.5 cm (0.1968 in) from the head, a circular hole is formed within 1 minute which is 1 cm. (0.3937 inch) in diameter, which is less than the 0.5 inch (1.27 cm) diameter of the emitting head.

When the foil is mounted at a distance of 0.85 cm. (0.2953 inch) from the head, it takes three times the exposure time to puncture the foil, and the hole has a diameter of 0.8 cm (0.288 inch).

This shows the very narrow pattern of energy distribution for this kind of transducer. At a distance of 1.8 cm (0.7087 in.) no hole is formed in a 12 minute exposure. The exposure of a painted surface showed a visible effect only at a very short distance.

(c) Tests with a complex large transducer.

Since this laboratory does not have a large transducer such as is used in ships, the characteristics of these large transducers were not known by the group until late in the contract period when some exposures were made with the cooperation of the U.S. Naval Applied Science Laboratory in Brooklyn, N. Y. Because the tests were made there, this group does not have all the instrumental details and all details about the position of each panel in front of the energy source; but a critical evaluation of the exposed panels establishes the following facts: these large transducers are so constructed that they emit bundles of concentrated radiation, each bundle similar to such a source as discussed under paragraph "b" but stronger in energy, and therefore the distance in which the bundle is effective is greater. When panels are exposed for approximately 24 hours in front of such a power source, they are hit by a bundle of concentrated beams which produces for each beam one cavitation area. Besides these individual bundles with their separate center effects, the whole bundle gives up some additional energy which spreads out from the center bundle to the sides and produces therefore effects over a wider area. When the transducer is mounted in the dome of a ship, the main bundle of energy will therefore hit the ship body straight ahead from the transducer source; but the side radiation will reach the wider area at the sides of the dome.

The tests at this time have shown that (1) the impact of the radiation in the center of each radiation beam causes cavitation-like, piercing results on the coating surface, with the degree of penetration varying with the hardness of the coating system. Hereby, a soft, poorly cured paint system of limited mechanical resistance, will show less cavitation effect, but the system will show other forms of failure. For instance, a special type antifouling paint over such a soft paint system will show extensive cracking over a wide area. On the other hand, a highly cross-linked system will show more cavitation effect but it will be visible also

that the radiation which is emitted from the center of the bundle is reflected and spread out over a wider area.

It is presently our aim to develop a modification of the coatings where the highly cross-linked experimental paints developed for the requirements of the adhesion factor are further extended to their cohesive properties.

The tests have shown (2) that it is evident that, similar as under "b", the center of each of the radiation beams is decreasing in diameter with the distance of the impingement area of the panel from the energy source. Although the panels which were exposed in the Naval Laboratory were mounted as nearly in similar position as possible, it is evident by comparison that the area of the radiation effects in the formation of cavitation varies between the panels from two square inches to three square inches; and at the same time the distance from one cavitation center to the other varies, with the varying area from cavitation to cavitation between  $2/16$  inch and  $3/16$  inch. More exposure tests and more evaluations will be required to establish the rate of energy distribution. Where the energy is spreading away from the center beam, different effects are to be obtained which are less of the cavitation type and more of the type as outlined under position "a" of this PART I.

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## II. THE FORMS OF FAILURE IN THE ADHESION TESTS UNDER VIBRATION.

Using conventional coating systems over pickled 1010 steel with an initial application of a wash-primer (Spec. MIL-P-15328 -Formula 117) followed by one coat of a top coat, and suspending the air dried panel in 5% saltwater under vibration, as outlined in PART I. pitting areas appear within 24 hours, especially in the lower part of the panel which is close to the entry area of the energy. These developing failures are not limited to the center area of the panel: smaller pitting developments become visible further up in the panel, covering about the whole lower half of the panel. At the same time the paint blisters off, not only from the lower edge but all along the sides of the panel, independent of the distance of the area from the entry of the vibration energy. By using the top-coat in a different color than the primer, the progress of these developments is clearly visible.

Using a different system, such as red lead vinyl primer MIL-P-15929 B, Formula 119, with a commercial neoprene paint ( N-39 Cold Bond ,Gates Engineering Co.) similar developments are visible over the whole area of the panel after 72 hours exposure. ( Reference:Figures 1 and 2, Letter Report No. 5)

In other paint systems, the failure appeared in the form of filament formations of increasing length, and peeling starting from the edge areas.

These developments differed from the results of other test methods, in particular the saltfog exposure results. It was necessary, therefore, to establish the reasons for these failures and to aim for an elimination of these defects.

Any paint system consists of the top coats, as well as of the primers, and the inter-face reaction area between the primers and the substrate, or the metal surface which is to be coated. In the paint system there are usually several different paints, such as an anti-fouling paint, several coats of the main paint

material used and the primer which is applied over a surface treatment or washprimer. Each of these coats is expected to have different hardness, and a different form or degree of curing; and between the various coating materials there is a different degree of inter-reactivity.

All these factors affect the uniformity of the applied coating system and, therefore, the degree of stability under the test conditions. One important factor, discussed in the Intermediate Progress Report of May 29, 1965, is the degree of solvent retention in each of the applied coats before the application of the next coat. TABLES 14-16 of that report gave data about varying film thickness caused by solvent retention under varying temperature and curing conditions. Also the effect of vacuum application was reported, and the effect of varying the solvent types in diluting the paint. When a paint system is built on a series of still-swollen layers, such as results from the retention of solvent, there is a continuing change in the inter-layer conditions when the coating system continues to age. Conditions arise, therefore, which are undesirable for the exposure in saltwater under supersonic vibration.

The systematic curing of the individual coats, and the partial replacement of toluene or xylene by 2 nitropropane improved the exposure results, as will be shown further-on.

If one coating material has a limited bond to the preceding material, the exposure tests will show a primary failure of that paint layer down to the next paint material. Especially, the anti-fouling paints were found to have a limited life over the main coating system.

The most important factor is the bond of the whole paint system to the metal base. If a failure occurs here, a peeling of the whole system takes place, followed by corrosion, usually starting from the edges. Therefore, the surface treatment, or the wash-primer coat, or the degree of bonding of the next primer to the wash-primer coat is of primary importance to the life of the adhesion of the paint system. This is further discussed in Part III.

### III. APPROACHES TO INCREASE THE ADHERENCE CONDITIONS.

The findings on the factors which influence the adherence conditions under the vibration test in 5% saltwater are being reviewed under the following aspects :

#### 1. A SYSTEMATIC SURFACE PREPARATION.

It is of primary consideration in any systematic building up of a maximum degree of adhesion for any paint system, that the system is anchored as well as possible to the substrate. Since it is known and since it can be recorded with the Brush Surface Analyser (Brush Electronics Company, Cleveland, Ohio) that any metal surface has, without systematic surface preparation, an irregular and not controlled surface profile, the desired maximum adhesion requires a systematic modification of that surface before paint application. This preparation consists of a removal of rust and oxide layers, and in the preparation of a new and regular surface profile. In the laboratory tests of this report, the surface was wire-brushed, and so a new surface was obtained having greater reactivity than would have been available in a partially or fully oxidized surface. On ships, such a surface preparation can start with sand- or grit-blasting of the surface.

After wire-brushing, the newly obtained surface was subjected to a chemical treatment with a rust-inhibiting pickle. It has been shown that such a rust inhibiting pickle produces a chemical reaction coating on the freshly wire-brushed steel. This has been shown by establishing the degree of chemical reaction coating as the "stripping weight per square foot" surface, which amounts to 16.2 mg/sq.ft. (More specific data is shown in the Intermediate Progress Report of the Project, Tables 1 and 2.)

Due to the low viscosity of the pickling solution it might be expected that the solution penetrated into the cavities of the profile, and that therefore the chemical surface modification was extended into such areas of "depth" in the metal profile. It might still be established in a future study how far the uniformity of such a penetration

might be influenced further by the addition of agents for increasing the wetting properties of the pickling solution.

Under the aspect of a chemically prepared surface, it is further to be assumed that all subsequent building up of a highly adherent coating system depends on the anchorage which is obtained between the newly prepared, chemically rust inhibited surface and the subsequent coats of the coating system.

Since the profile-depth areas, or the cavities of the profile, have been chemically modified without filling these areas, the continued systematic build-up of a fully anchored paint system, still requires that the first primer coat should continue to include the profile cavities in the coating process. One way is the application of the wash-primer MIL-P-15328 B, which is of low viscosity and is reactive with the substrate. Here again, future studies should include how far this uniform reaction in the surface cavities can be increased by the use of wetting additives in the wash-primer type coating. But such a systematic preparation can be assumed to give the substrate surface a quite well modified state.

Applying now a heavier primer coating, such primer should be based on reactive pigments and should have maximum flow properties in covering all areas of the profile. That reactive pigmentation has an influence on the inter-reaction in the build-up was shown in the Intermediate Progress Report, Table 3, when it was shown that a diluted, red lead-linseed oil primer caused an increase of the stripping weight over that obtained by the rust inhibiting pickle. That the degree of wetting influences the stripping weight increase was shown, also in the same Table 3, when a change in the diluent from Xylene to 2 Nitropropane caused also an increase in the reaction coating on the steel. It has been shown throughout the work that a red lead vinyl primer MIL-P-15929 B over a wash-primer surface causes a further increase in the reaction coating weight.

Reviewing at this time the knowledge which has been obtained, it appears that

in future work, studies should be made on how far the flow of the vinyl primers (red lead or zinc chromate vinyl primers) might be influenced further by the use of systematic additives, and how far this would result in a still more uniformly developed inter-linkage and adhesion stability.

TABLE 5 in this report gives the factors which have been reviewed up to this time. New factors, which have been studied in the report period, are tabulated in TABLE 6. They refer to the following:

a) the temperature of the pickling solution. The fact that TABLE 6 shows a higher weight of the reaction coating with the increase in temperature of the pickling solution is assumed to have two reasons: one is the increase of the reaction in a hot solution; the other is the degree of air removal from the cavities of the metal profile with increasing penetration of the pickling solution into the cavities. This results in a more complete chemical surface modification. In ship practice, the pickling might be considered by a hot-chemical, surface-modifying spray application.

b) the selection of the complex-forming metal component in the pickling solution. TABLE 6 shows that the otherwise same solutions increase in the resulting weight of the reaction coating with the variation with a sodium dichromate pickle, and a sodium molybdate pickle, eventually under the addition of a ceric sulfate agent. Other factors which have been considered are the introduction of metallic zinc into the primer.

It has also been observed that a wire-brushed surface might be flame-oxidized before the application of a hot pickle, whereafter a further increase in stripping weight has been observed. This had been reported in more detail in Letter Report No.19.

For the purpose of uniformity, in most paint applications in this report the standard rust inhibiting pickle was used hot, which gave satisfactory results with the various systems.

TABLE 5.

FACTORS OF A SYSTEMATIC SURFACE PREPARATION

1. ESTABLISHING A SURFACE PREPARED FOR MAXIMUM PAINT ADHERENCE:

a) REMOVAL OF ADHERENT RUST AND OF OXIDATION LAYERS BY

EITHER WIRE-BRUSHING OR

BY SAND (GRIT) BLASTING.

SIMULTANEOUSLY OBTAINING A MORE UNIFORM PROFILE OR NETWORK BETWEEN CAVITIES

AND SURFACE LAYERS.

b) MODIFYING THE EXPOSED SURFACE IN ALL AREAS BY CHEMICAL TREATMENT

BY THE USE OF A RUST INHIBITING PICKLE ( LOW VISCOSITY, PENETRATING AND

REACTIVE)

2. APPLICATION OF WELL ANCHORED PRIMERS.

a) USING A REACTIVE LOW VISCOSITY WASH-PRIMER MIL-P-15328 B, WHICH IS REACTIVE WITH

STEEL AND IS INTER-REACTING WITH THE LOW STRIPPING WEIGHT REACTION COATING

WHICH RESULTS FROM THE RUST INHIBITING PICKLE.

b) OR APPLICATION OF REACTIVE OIL PRIMER, SUCH AS RED LEAD-LINSEED OIL

PRIMER IN A FORM WHICH IS NOT TOO VISCOUS TO PENETRATE INTO THE PICKLED

"CAVITIES" OF THE PROFILE.

A SECOND PRIMER COAT CAN BE OF HIGHER VISCOSITY, IF USED.

3. APPLICATION OF VARIOUS COATING SYSTEMS OVER THE WASH-PRIMER ( 2-a):

a) APPLICATION OF RED LEAD VINYL PRIMER ( MIL-P-15929 B, Formula 119) OR

ZINC CHROMATE VINYL PRIMER ( MIL-P-15930 B, Formula 120), AIMING FOR GOOD

ADHERENCE TO THE PRECEDING WASH-PRIMER.

b) SUBSEQUENT APPLICATION OF VARIOUS SPECIFICATION PAINTS, OR NEW EXPERIMENTAL

PAINTS AS DISCUSSED LATER IN THIS REPORT.

TABLE 6.

## NEWLY STUDIED FACTORS IN REACTING THE METAL SURFACE

A) USED: RUST INHIBITING PICKLE (from TABLE 1, INTERMEDIATE REPORT), AT VARYING TEMPERATURE.

THE PICKLE: A SOLUTION WAS MADE OF 5.86 g.  $\text{Na Cr}_2\text{O}_7$

I. AND 5.59 g. PHOSPHORIC ACID 85%

IN 400 ml. WATER.

ANOTHER SOLUTION WAS MADE OF

II. 25 g. SULFURIC ACID

AND 225 g. WATER.

TO THIS SOLUTION II

10 g. OF SOLUTION I WERE ADDED.

TREATMENT	WEIGHT: BEFORE STRIPPING	AFTER (g)	WEIGHT LOSS mg.	AREA sq. in.	STRIPPING WEIGHT mg/sq. ft.
SAE 1010 STEEL IMMERSED IN STANDARD PICKLE AT R.T.	109.0888	109.0865	2.3	34.0	10.0
SAME PICKLE, INCREASING THE REACTIVITY WITH 0.5% SELENOUS ACID AT R.T.	110.4764	110.4721	4.3	34.0	18.2
USING THE STANDARD PICKLE NEAR BOILING TEMPERATURE.	110.1126	110.1085	4.1	13.5	43.6

B) VARYING THE COMPLEX FORMING COMPONENT IN THE PICKLING SOLUTION (NEAR BOILING POINT).  
WITH REGULAR PICKLE  
(SODIUM DICHROMATE)

REPLACING THE SODIUM DI- CHROMATE BY SODIUM MOLYB- DATE (SAME AMOUNT)			9.0	20.62	62.8
---	--	--	-----	-------	------

SAME, BUT ADDING 5 ml. OF A SOLUTION OF 1 g. CERIC SULFATE IN 100 ml. SULFURIC ACID (10%).			10.9	20.62	69.3
--	--	--	------	-------	------

REPLACING THE SODIUM DICHROMATE BY 5 g. MOLYBDENYL ACETYL ACETONATE.			9.5	20.62	66.4
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APPROACHES TO INCREASE THE ADHERENCE CONDITIONS:(Continued)

2. BY INCREASED INTER-REACTION BETWEEN THE SURFACE OF THE METAL AND THE FIRST COAT.

This Section 2 continues basically the principles outlined in the preceding Section 1; but here the primers are applied to the mechanically prepared and chemically pickled surfaces. In TABLE 5 it has already been pointed out that either a reactive pigment/oil primer can be used in a diluted form so that it will penetrate into the cavities of the profile and will inter-react there; or, the specification wash-primer MIL-P-15328, Formula 117, can be used, which is of low viscosity, penetrating quality and surface reacting. In these cases the system can continue with the application either of a red lead vinyl primer (MIL-P-15929 B, Formula 119) or a zinc chromate vinyl primer (MIL-P-15930 B, Formula 120). In all these cases the primer can inter-react chemically with the chemically modified metal surface of the preceding Section 1.

Some data which substantiate this are shown in TABLE 7.

In the second part of TABLE 7 it is interesting to note that the stripping weight did not notably increase when zinc dust was added to the red lead vinyl primer. This is assumed to be caused not by a lack of reactivity of the zinc component, but rather by a lack of penetration of the highly pigmented paint into the cavities of the surface profile. This results in a lesser degree of chemical inter-reaction in these areas. That, in the same Table 7, the addition of aluminum decreased the resulting reaction coating, in spite of the use of low viscosity dispersing agent for the aluminum, is due to the very low degree of reactivity of the aluminum in these systems.

Reviewing at this state again the adhesion under vibration of these primer systems, it is a repeated observation that an application of the red lead vinyl primer over wire-brushed steel without and with pickling has, under 5% saltwater exposure in the first of the described test systems for the effect of supersonic vibration ( "a", on page 4 ), a very poor life before the vinyl primer film loses its adherence

TABLE 7

THE CHEMICAL INTER-REACTION OF A REACTIVE PRIMER WITH THE PRE-TREATED  
SURFACE UNDERNEATH

STEP I. HOT PICKLING OF WIRE-BRUSHED STEEL: STRIPPING WEIGHT OF THE REACTION COATING.

WEIGHT BEFORE STRIPPING (grams)	AFTER	WEIGHT LOSS mg.	AREA Sq. in.	STRIPPING WEIGHT mg/sq. ft.
110.1126	110.1085	4.1	13.5	43.6

STEP II. AFTER APPLICATION OF WASH-PRIMER (Spec. MIL-P-15328, F.117) OVER HOT PICKLED  
STEEL

73.0533	73.0464	7.0	16.5	61.4
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STEP III. AFTER APPLICATION OF THE RED LEAD VINYL PRIMER (MIL-P-15929 B, F.119) OVER THE  
WASHPRIMER

72.9275	72.9192	8.3	16.5	72.15
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INFLUENCE OF METAL ADDITIONS TO THE RED LEAD VINYL PRIMER ( F. 119)

a) ADDING TO 500 g. VINYL RED LEAD PRIMER  
112.5 g. ZINC DUST #22 (New Jersey Zinc Co.):

72.9166	72.9082	8.4	16.5	73.1
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b) ADDING TO 200 g. RED LEAD VINYL PRIMER  
25 g. ALUMINUM 5 XD (Reynolds Metals Co., Louisville, Ky.)  
(DISPERSED IN METHYL ISO-BUTYL KETONE)

72.9870	72.9795	7.5	16.5	64.0
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to the steel and peels off from the edges. The same primer over hot pickle and wash-primer maintains this adhesion for a much longer time and any failure which begins to develop afterwards is in the form of local pitting or filament formation rather than a straight loss of the film adherence.

The pitting formation proceeds then somewhat faster when the zinc chromate vinyl primer (MIL-P-15930 B, Formula 120) has been applied than in the case of the red lead vinyl primer of MIL-P-15929 B, Formula 119. ( Reference:Letter Report No. 16, Fig. 1)

That is why often in Naval practice both primers are being applied successfully instead of two coats of one type.

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## APPROACHES TO INCREASE THE ADHERENCE CONDITIONS (Continued)

### 3. THE ROLE OF SOLVENT RETENTION IN THE PAINT SYSTEM.

It has been pointed out in the Intermediate Report that the factor of solvent retention in multi-coat paint systems is a factor to be considered in the stability of paint systems under saltwater and under vibration conditions. Any paint coating represents a formation which has the tendency to retain sweller material, or solvent residues, in the paint layer. Upon aging, or under temperature variations the retained solvent is gradually being driven out. This results in a decrease in the volume of the paint layer and produces, in the case of a multi-layer coating system, pressure on the underlying coat. Exposure in saltwater adds the additional factor that the saltwater tends to penetrate in the coating system; and, depending on the degree of curing or on the decrease in solvent retention, increases the resistance of the coating against the saltwater penetration. The factor of exposure then to supersonic vibration under saltwater further accelerates the paint failure and the loss of adherence between the various coats and between the whole system and the substrate.

In the first year's work of the contract, the considerable amount of solvent retention in a vinyl system was determined. It was shown that the total coating thickness varied for an application with an air-drying of all coats vs. an application of 15 minutes exposure to 90<sup>o</sup> Centigrade for each coat. It was shown that the panel with the highest amount of retained solvent and a coating thickness of 30 mils had large pinholes and blisters after 40 hours exposure in 5% saltwater with supersonic vibration, when a corresponding panel with increased curing had a total film thickness of 26 mils and was in good condition after the same exposure test. ( Ref:Intermediate Report, Tables 14 and 15).

During the further work, we proceeded to the use of coatings containing highly cross-linked vehicles or containing elastomeric polymers in the vehicles.

It is known that any polymer with an increased degree of polymerization increases also in the gel properties. Also, every gel is characterized by its swelling with solvents. Hereby, the solvent penetrates into the gel network and will find a greater resistance to complete evaporation from this state. Therefore the importance of this point has increased further in the new coating developments. It has been pointed out ( Interim Progress Report, Tables 17 - 19 ) that a solvent such as 2 nitropropane shows less retention of solvent in the coatings than, for instance, xylene or toluene. Therefore, some of this material has been included in the experimental coatings , which are discussed in PART IV of this report, and the results continued to be satisfactory. It is especially important to consider the influence of solvent retention when coatings of different chemical character are being applied on top of one another. When the final coat, for instance an anti-fouling paint coat, has less solvent retention than the elastomeric coatings underneath, the vibration test shows , in exposure to 5% saltwater and vibration, a peeling of the anti-fouling paint from the underlying system. Using anti-fouling paint and the main paint system in different colors, the underlying system appears quite quickly upon exposure to supersonic vibration when the anti-fouling paint is not fully bound together in a joint system with the main paint system.

There is still another factor which has not been fully and clearly established. It is known in the field of electrical insulation applications that in applying a coating of lower content of sweller, or plasticizer, over a coating with a higher content of sweller, a migration takes place of the sweller ( plasticizer) from the material with the higher content of swelling matter to the material with the lower content of swelling matter. A similar phenomenon can be expected to take place between the ship coatings also. If the last coat under these conditions should have turned very hard, it might develop the formation of surface cracking. This

form of paint failure has been observed in recent studies using a polyisobutylene anti-fouling paint over a commercial neoprene paint system. In any development of complete paint systems, including new anti-fouling paints, this factor must be taken into consideration.

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APPROACHES TO INCREASE THE ADHERENCE CONDITIONS (Continued).

4. A SYSTEMATIC INCREASE IN CROSSLINKING IN THE COATINGS DURING THE CURING.

In the usual practice the various coating materials have been identified according to their film-forming vehicles and their pigmentation. The general specifications give no indication about the degree of polymer properties in such materials. They do not refer to the degree of the progressing polymerization which is taking place during the curing of the applied coating. It must be understood that the vehicle of such paints might contain some materials which are polymerized to a certain degree and that those materials might, upon drying or curing, progress in their polymer state; for instance, alkyds in vehicles or phenolic resins in vehicles belong to this group. Other vehicles might contain elastomeric components, such as neoprene or polyisobutylene, which contain polymer matter to a certain per centage. These elastomeric components usually progress only slightly in their polymer state upon air drying of such coatings.

All these progressing steps in the polymerization of coatings can be influenced chemically in an effort to produce more highly crosslinked or denser polymer films, or films of greater resistance to solvent swelling or to saltwater penetration.

(a) Increased crosslinking in alkyd resins:

It is to be understood that every polymer material which is being introduced in the coating system consists for itself of highly polymer, insoluble-but-swelling matter together with low polymer or still-not-polymer matter, which acts as a sweller in the polymer material which is being used in the preparation of the coating material. Therefore, these polymers are mixed-phase or heterophase substances. A chemical increase of the high polymer phase in the paint increases the characteristic polymer properties of the coating.

The project director has studied this in the case of oil modified alkyd resins such as used in Navy paints, in a paper which has been presented during the project. (Reference: American Chemical Society, Division of Organic Coatings and Plastics Chemistry, Preprint Book, "Papers Presented at the Detroit Meeting", Vol. 25, No. 1, pages 105-115, April 1965). While that particular study had been a part of the work under Grant GP-929 of the National Science Foundation, some of the findings are important for the work approach of the present study. It has been shown in said paper that a long oil soya modified alkyd resin, according to Specification TT-R-266a, such as the commercial AROPLAZ 1266 M 70, has in its initial form (such as is being used in the preparation of a specification paint) only a small ratio of three dimensional polymer matter. That is why the electron diffraction spectrum of that alkyd has the usual halo pattern. When, however, such an alkyd is further cured in a coating, such as by heating 16 grams alkyd solution (70%) with 0.65 gram t butyl perbenzoate, a new polymer matter is being formed. Since any oil modified alkyd according to said specification represents a combination of materials, its resulting polymer has similar properties as polychrystalline units have. They show in their electron diffraction spectra under different stomic orientation with different angles of the electron beam also different spectra. (See FIGURES 6, 8 -10 of above pre-print paper)

Going one step further, it is to be considered that in a specification alkyd paint the vehicle might contain other components also; and these can contribute to the reactions which take place in the curing of the paint. To establish this fact, the same paper used as an example a mixture of the same alkyd with a basic zinc octoate, that is, a material of the group of the usual octoate driers. When this mixture was heated with the t butyl perbenzoate and the new polymerization product was isolated, a completely different electron diffraction spectrum was obtained. (See Figure 15 of above pre-print paper).

This new product was then divided into a phase which is soluble in boiling benzene and another phase which is not soluble in boiling benzene. The phase solids were in this form isolated and studied under the electron microscope. (See FIGURES 16 and 19 of said pre-print paper). Fully different patterns were obtained for each phase and different also from the initial alkyd itself. In this form it has been established that each alkyd vehicle can be changed chemically by progressing polymerization or sustained cross-linking. The resulting paint is then not only a product of surface drying but is chemically modified throughout its mass. That is why new and desirable properties can be given to such alkyds by systematic crosslinking, and it is of great importance in what form such paint vehicles are when they are applied to the ship.

(b) The increased crosslinkage of elastomeric vehicles.

It has been studied how far this basic approach can be used on the chemical cross-linking of elastomers, such as neoprene, or polyisobutylene, or others. This research group has shown earlier that all elastomers represent mixed phases, or heterophase polymer materials, in which the ratio of the three dimensional phase to the low polymer and still-soluble phase produces the properties of each elastomer. (1) In most elastomers the percentage of the insoluble phase is considerably lower than, for instance, in thermosetting resinous polymers; and since these elastomers have a considerable capacity of swelling in solvents, the concentration of an elastomer in a so-called solution is usually low. Within this elastomer, therefore, the concentration of the high polymer phase in the solution is very low. Therefore, the paints based on such solutions harden slowly and not to a fully satisfactory degree. It is necessary, therefore, to develop methods for their additional cross-linkage in the produced paints, in the state preceding their application as well as after the application of these paints.

In the Intermediate Progress Report of this project (May 29, 1965) this

cross-linking was studied in the case of neoprene, using tetra alkyl titanates or their epoxide derivatives as cross-linking agents. (The preparation of such an epoxide was described by Kronstein, Carroad and Byrd in an earlier paper which has been published in the OFFICIAL DIGEST, Vol. 37, No. 482, page 284, March 1965.)<sup>(2)</sup> The Intermediate Report gave photos of the cross-linking effect in neoprene in FIGURES 2 to 7 of said report. This cross-linking effect is not limited to neoprene, however, or any other specific elastomer. This group has not been able to find any kind of elastomer as yet, which did not follow similar patterns of increased cross-linkage. Even natural rubber follows the same pattern when a rubber "solution" is reacted with a tetra octyl titanate (Ref: FIGURES 1, 2 and 3 in JOURNAL OF PAINT TECHNOLOGY, Vol. 38, No. 492, pages 38-39, January 1966)<sup>(1)</sup>, and the polymer phase is being precipitated. Upon re-swelling, such polymers form films. Similar cross-linking effects have been established on a number of synthetic rubbers such as styrene-butadiene rubber, butadiene-acrylonitrile rubber, Thiokol, butyl rubber, silicone rubber, and other elastomers such as vinyl chloride/vinylidene chloride, and polyvinyl acetate.

These basic findings have been used in the experimental paints which are being listed later-on. It has been established in this present work that such polymers can continue to harden by extended cross-linkage to a state where they obtain a glass-like hardness. It is presently under study how this hardness can be controlled to reach and maintain the required optimum. Two approaches are under study: the use of a limited amount of plasticizer such as tricresyl phosphate or the incorporation of a limited amount of a less hardening type of a synthetic rubber, such as is known in the industry as liquid rubber forms. Under study here is a very low molecular weight copolymer of butadiene and acrylonitrile with a medium-high acrylonitrile content. This is still under development.

APPROACHES TO INCREASE THE ADHERENCE CONDITIONS. (Continued)

5. AIMING FOR AN ADDITIONAL DEVELOPMENT OF AN ADHERENT ANTI-FOULING PAINT.

It is the present practice to apply in ship use one or two coats of anti-fouling paint to any paint system, without consideration how far these final coats are chemically and physically inter-linking with the main paint system. These anti-fouling paints have been developed primarily as a suspension of a large percentage of pigments with toxic properties. The vehicle has here the primary purpose of forming enough film characteristics to hold the high concentration of toxic pigmentation to the surface of the coating system. The vehicles are generally so selected as to have limited coherence and limited underwater life, so that on deterioration the toxic pigment might be released. For example, the anti-fouling paint Formula 121/63 is using 1440 lbs. cuprous oxide with 55 lbs. vinyl chloride-acetate copolymer, or using 100 lbs. pigment with 3.8 lbs. film former. To extend the film former, 215 lbs. pine rosin is added, which is included in the paint film without having any film forming properties for itself. Since this mixture is too brittle, 50 lbs. tricresylphosphate is added as a softener. The resulting paint film is in its composition contrary to all general principles of an underwater top coat, but it releases during its deterioration large amounts of cuprous oxide.

When exposed directly to the power of strong transducer energy, this energy pierces the coating quickly and the underlying paint is being exposed.

Similar is the basic composition and general behavior of anti-fouling paint Formula 134\*, where polyisobutylene is used as film former and where the ratio of film former to cuprous oxide pigment is somewhat higher than in Formula 121/63. Here 45 lbs. polyisobutylene polymer is used with 700 lbs. cuprous oxide, hardening this mixture with 32 lbs. pine rosin. This is a ratio of 6.43 lbs. film former to 100 lbs. toxic pigment. but here still the film is so hard that under

\*MIL-P-22299 (SHIPS)

direct exposure to the transducer energy, the radiation energy pierces the anti-fouling paint layer readily down to the underlying paint system.

In aiming for a new and systematic paint system, which produces the maximum resistance under adhesion in the range of supersonic vibration two new approaches have been traced, although it was not possible to pursue the development of new anti-fouling paints within the scope of the present work. These refer to (a) producing a high polymer vehicle binder for toxic pigmentation and (b) to incorporate into this polymer vehicle metalorganic components which have toxic properties. Such vehicles can then be pigmented with toxic pigmentation besides the toxic properties of the vehicle.

Especially, tin organics have been explored. The difficulty was at this time to find a method to determine the rate of toxic release under saltwater and under supersonic vibration exposure. The vehicles which have been tested at the present time and using tin octoate as a part of the metalorganic part of the polymer complexes had such a long saltwater life under vibration conditions that time did not allow coming to definite results about its toxic release. This problem of anti-fouling paints will have to be pursued for itself.

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#### IV. DESCRIPTION OF THE PRE-TREATMENTS AND COATINGS USED.

In the following tables the composition is listed of the materials which were used in this work:

- (a) TABLE 8 lists some of the pickling solutions, either according to Navy practice, or modifications, and new solutions; but in all cases the purpose is the same, to produce a reactive solution of low viscosity which is capable of penetrating all parts of the surface, including the profile cavities fully and to produce there a new reaction layer, which seals the earlier deoxidized surface against new oxidation until the next treatment is being applied.
- (b) TABLE 9 lists reaction primers, including the specification wash-primer, whose purpose is to continue the reaction coating build-up on all parts of the surface, again, including its cavities. The Table shows three different groups of "wash-primers". But again it is to be pointed out that with respect to the basic approach of reactive primer-coat formations over all areas of a profile many other formulations are possible.
- (c) TABLE 10 gives vinyl primers, which can be applied over these pre-treated and wash-primed surfaces. It is possible to apply this type of primer in two coats, where by the first coat might be used in a more diluted form to facilitate the anchorage in the profiles of the surface. It is possible also to use one coat of a red lead vinyl primer followed by one coat of zinc chromate vinyl primer, or in a reversed order. TABLE 10 refers also to the fact that such a primer can be combined with a metal powder, either zinc dust or aluminum. In the case of the zinc dust the corrosion resistance might be satisfactory, but the penetration into the cavity areas of the surface is more difficult with such a combined pigmentation and therefore in the tests of the Table did not show increased stripping weight over the same primer without the addition of zinc dust.

FORMULATIONS USED IN THE CURRENT REPORT PERIOD (I.)

TABLE 8

INHIBITING SURFACE PICKLING SOLUTIONS

THE STANDARD PICKLING SOLUTION:

- a) 5.9 g SODIUM DICHROMATE  
5.6 g PHOSPHORIC ACID ORTHO 85%  
IN 400 g WATER
- b) 25 g SULFURIC ACID CONC  
225 g WATER
- c) 10 g SOLUTION a ADDED TO 250 g SOLUTION b

USED: SOLUTION AT R.T. AND

SOLUTION NEAR BOILING POINT: DIFFERENT EFFECTS SHOWN IN TABLE 6

USED IN MOST OF THE SUBSEQUENT APPLICATIONS: NEAR THE BOILING POINT.

MODIFICATIONS USED:

- 1) ADDING 0.5 % SELENOUS ACID (AT R.T.)

EFFECT IN INCREASING REACTION COATING WEIGHT ( AT R.T.)SEE TABLE 6-A

- 2) USING SODIUM MOLYBDATE INSTEAD OF SODIUM DICHROMATE

EFFECT IN INCREASING REACTION COATING WEIGHT ( NEAR BOILING POINT)

SEE IN TABLE 6 - B

- 3) PREPARING PART a IN THE STANDARD SOLUTION FROM: 5 g MOLYBDENYL ACETYL  
ACETONATE  
5 g PHOSPHORIC ACID  
400 g WATER

EFFECT ON COATING WEIGHT (NEAR BOILING POINT) SEE TABLE 6 -B

FORMULATIONS USED IN THE CURRENT REPORT PERIOD ( II )

TABLE 9

a) REACTION PRIMERS USED IN THIS WORK PERIOD

THE SPECIFICATION WASHPRIMER MIL-P -15328 B (FORMULA 117)

INFLUENCE ON THE PRECEDING PICKLING LAYER IN TABLE 5

INCREASING EFFECT ON THE REACTION COATING IN TABLE 7 STEP II

THIS MATERIAL WAS USED IN MOST TESTS AS WASHPRIMER

b) A COMMERCIAL EPOXY TYPE WASHPRIMER BASED ON SHELL'S EPONOL 55 RESIN

THE FORMULATION WAS GIVEN IN THE INTERMEDIATE REPORT ,TABLE 27 - II

c) A DIFFERENT REACTION PRIMER USED OVER THE PICKLE:

( CODE V-2-85) 15 g MOLYBDENYL ACETYL ACETONATE

IN 500 mls ACETONE

75 g ALKYDRESIN (AROPLAZ 1266 - M 70)

THE PANELS WERE DIPPED FOUR TIMES AT 30 SEC.INTERVAL

ON WIPING THIS COATING OFF WITH TOLUOL A BROWNISH -BLUE REACTION LAYER WAS  
EXPOSED.

WHEN A VINYL PRIMER AND A TOPCOAT WAS APPLIED OVER THIS M.A PRIMER, THE RESULTING  
TOTAL FILMTHICKNESS WAS THE SAME AS WHEN THE STANDARD WASHPRIMER a) HAD BEEN USED.

OTHER EXPERIMENTAL FORMULATIONS HAVE BEEN USED ALSO.

FORMULATIONS USED IN THE CURRENT REPORT PERIOD(III)

TABLE 10

VARIOUS FORMS OF VINYL PRIMERS

- a) THE RED LEAD VINYL PRIMER MIL -P-15929 B FORMULA 119
- b) THE ZINC CHROMATE VINYL PRIMER MIL-P-15930 B FORMULA 120
- c) APPLICATIONS OF BOTH THESE PRIMERS
- d) EXPERIMENTAL ADDITIONS OF ZINC POWDER TO RED LEAD VINYL PRIMER

112.5 g ZINC DUST # 22 TO

500 g VINYL RED LEAD PRIMER a)

INFLUENCE ON STRIPPING WEIGHT SEE TABLE 7

- e) EXPERIMENTAL ADDITION OF ALUMINUM POWDER TO RED LEAD VINYL PRIMER

200 g RED LEAD VINYL PRIMER

20 g ALUMINUM 5 XD (PREDISPERSED IN METHYL ISOBUTYL KETONE)

INFLUENCE ON STRIPPING WEIGHT SEE TABLE 7

TESTED AGAINST # a(OVER PICKLE AND WASHPRIMER)

( THE PICKLE USED WAS THE MODIFICATION 1) OF TABLE 8)

AFTER TEST IN WITH RED LEAD VINYL PRIMER  
5% SALTWATER UNDER  
SUPERSONIC VIBRATION

WITH RED LEAD /ALUMINUM # e

AFTER 90 HOURS VERY GOOD CONDITION

GOOD CONDITION, BUT ONE  
SMALL PINHOLE

AFTER 106HOURS GOOD CONDITION WITH  
SEVERAL SCATTERED FINE  
PINHOLES

FIVE TO SIX PINHOLES ON  
EACH SIDE OF PANEL

NOTE THAT THE ALUMINUM HERE DID NOT IMPROVE THE PROTECTIVE EFFECT.

THE BEST ADHESION EFFECTS WERE OBTAINED WHEN PANELS AFTER PICKLING, WASHPRIMER AND TWO COATS OF VINYL PRIMER a) OR b) ( OR a) AND b) ) WERE EXPOSED TO AN ELEVATED TEMPERATURE FOR 15 MINUTES .

The primer with aluminum decreased in stripping weight due to the low reactivity of the aluminum component.

(d) The subsequent TABLES 11 - 14 give various experimental top coats. TABLE 11 lists the fact that comparative tests were made with the specification grey vinyl alkyd enamel MIL-E-15936 B ( Formula 122-27). This was used because a combination of a vinyl resin and alkyd system produces a very dense polymer coating. This group has worked with this type of enamel in earlier years.

The first of the experimental paints is based on the findings of this research group: a) that any drying oil can be heated under air-blowing, or with organoperoxide treatment into a gel state, where it is no longer capable of forming a stable solution. But by further heating the gel with metalsoap compounds, the gel is being dispersed and forms a stable form which can be diluted further with organic solvents, without losing its high-polymer components. It is referred to as varnish "G"

b) that high-temperature stable compounds can be produced by a complex formation between a tetra alkyl titanate and a metal octoate

c) that compounds of positions a) and b) can be mixed and can be co-polymerized with the use of a titanate epoxide as cross-linking agent. The resulting compound can be dispersed in solvents and can be pigmented and produces highly stable and highly cross-linked coating materials.

TABLE 12 gives a second experimental paint whose vehicle contains the same complex matter as Position a) of TABLE 11, but the metal-octoate component is not first vacuum distilled with a tetra alkyl titanate. The octoate is added directly to the varnish "G" and the mixture is again cross-linked with a titanate epoxide.

FORMULATIONS USED IN THE CURENT REPORT PERIOD ( IV. )

TABLE 11

TOPCOATS USED IN THE PRESENT PERIOD

a) SPECIFICATION PAINT ( IN COMPARATIVE TESTS ) :

EXTERIOR GRAY VINYL ALKYD ENAMEL : MIL-E- 15936 B      FORMULA 122 -27

b) EXPERIMENTAL DEVELOPMENTS:

I. PRE-GELLED LINSEEDOIL REDISPERSED IN COBALT DERIVED LINSEEDOIL METAL SOAP

REFERRED TO VARNISH " G "

ACCORDING TO U.S.PATENT 2,476,879<sup>(3)</sup> AND 2,568,550<sup>(4)</sup> (MAX KRONSTEIN)  
AND TO "PAINT AND VARNISH PRODUCTION" MAGAZINE VOL.50 No.4 APRIL 1960<sup>(5)</sup>  
TABLE 3-a

II. METALORGANIC GROUPINGS INTRODUCED STARTING FROM A REACTION PRODUCT OF

TETRA ALKYL TITANATE AND BASIC ZINC OCTOATE

ACCORDING TO U.S.PATENT 3,196,166<sup>(6)</sup> (M.KRONSTEIN AND WILLIAM KAPFER)

ASSIGNED TO THE U.S.SECRETARY OF THE NAVY

III. REACTION PRODUCTS BETWEEN I AND II

EXAMPLE : 70 g OF No.II

100 g OF A 50% DISPERSION OF # I IN MINERAL SPIRITS OR XYLENE  
HEATED WITH 70 g TITANATE EPOXIDE (OBTAINED FROM VACUUM DISTILLA-  
TION OF 200 g TETRA ISOPROPYL TITANATE WITH 400 g VINYL CYCLOHEXENE  
DIOXIDE, KNOWN AS EPOXIDE 206)

REACTION PRODUCT REDISPERSED IN 200 g BENZENE

THIS DISPERSION CAN FURTHER BE COMBINED WITH NEOPRENE/BENZENE DISPER-  
SIONS.

IT CAN BE PIGMENTED WITH PIGMENT PASTES DISPERSED IN DEHYDRATED CASTOR-  
OIL U.A.

A CONSIDERABLE NUMBER OF EXPERIMENTAL VARIATIONS HAVE BEEN STUDIED.

FORMULATIONS USED IN THE PRESENT PERIOD (V)

TABLE 12.

TOP COATS USED IN THE PRESENT PERIOD.

b) EXPERIMENTAL DEVELOPMENTS (CONTINUED):

CONTINUATION TO I/II/III OF TABLE 11.

USED IN EXPERIMENTAL EVALUATION AS CODE # V-3-52

a) VEHICLE PREPARED FROM : 250 g VARNISH "G", THAT IS, EXPERIMENTAL  
STEP I OF TABLE 11

WITH 100 g TIN OCTOATE ( USED AS TIN ORGANIC COMPONENT)  
100 g ZINC OCTOATE, BASIC ( SUCH AS USED IN II/TABLE 11)  
140 g TITANATE EPOXIDE ( AS USED IN III/ TABLE 11)  
20 g BENZENE.

b) PIGMENT PASTE: 370 ZINC MOLYBDATE ( AS REACTIVE PIGMENT)

185 g RUTILE TITANIUM DIOXIDE R-750

185 g CALCIUM MOLYBDATE

(7)  
( THIS MIXTURE IS ACCORDING TO A PAPER BY M.KRONSTEIN  
AND COWORKERS, IN PRE-PRINTS OF THE DIVISION OF  
ORGANIC COATINGS AND PLASTICS CHEMISTRY, AMERICAN  
CHEMICAL SOCIETY, Vol. 25, No. 2, p. 173 (Sept.1965)

DISPERSED IN 51 g TUNG OIL

51 g DEHYDRATED CASTOR OIL (CASTUNG-103)

AND 112 g ALKYD RESIN (AROPLAZ 1266 M 70)

50 g 2 NITROPROPANE

c) PAINT PREPARED FROM 650 g PASTE b)

150 g VARNISH a)

7 g COBALT NAPHTHENATE 6% Co

35 g 2 NITROPROPANE

100 g OF A 1:1 MIXTURE OF VARNISH a) AND  
2 NITROPROPANE.

THE DRYING WAS ACCELERATED BY HEATING THIS PAINT: 40 g PAINT AND  
2 g TITANATE EPOXIDE

TO 100° C. FOR SHORT TIME.

In the paint of TABLE 12 two different metal-octoates are being used, a zinc octoate and a tin octoate, because here the tin organic component might be of interest in anti-fouling paint applications. This last point has not been investigated by this group as yet. As pigmentation, the paint of TABLE 12 uses the same zinc molybdate and calcium molybdate-titanium dioxide pigmentation as used by this group in an earlier work, because this combination has been found to have a reactive influence on the substrate, wherever any substrate material might be exposed.

TABLE 13 gives in the upper part still another modification of these approaches. In the lower part of TABLE 13 another new development is being introduced: the need for elastomer coatings had been indicated theoretically; but the earlier developments used as the elastomer usually neoprene, and this material is very difficult to disperse in solvents to any degree of high concentration. That is why known neoprene paints were low in polymer solids and required many coating applications. Such a multi-layer application of a swollen polymer brings the danger of extensive solvent retention in the film. Such coatings are very pliable, but not hardened, and any advantage which they might have is lowered by this low degree of hardening. That neoprene can be cross-linked by titanate epoxide and by various tetra alkyl titanates has been shown in the Intermediate Progress Report of this contract.

Now another approach was used: Another elastomer was used, which is dispersible in solvents to a much higher degree. A 25% solution of a chlorosulfonated Polyethylene (HYPALON 30) was used with the easily evaporating benzene as dispersing agent. As an additional cross-linking component a pre-cooked varnish based on a phenolic resin and tungoil, or of tung oil and linseed oil, was used, which is in accordance with Specification MIL-V-1137 A. As shown in TABLE 14, this resulting vehicle was pigmented with the ball-milled paste obtained from an activated carbon and synthetic iron oxide with an alkyd resin as vehicle and 2 Nitropropane as diluent. Hereby, it was of interest that the results were more stable with an activated carbon than

FORMULATIONS USED IN THE PRESENT PERIOD (VI)

TABLE 13

TOPCOATS USED IN THE PRESENT PERIOD

b) EXPERIMENTAL DEVELOPMENTS (CONTINUED)

MORE DEVELOPMENT TO THE SYSTEM I/II/III OF TABLE 12

A) THE VEHICLE a WAS PREPARED ALSO FROM

250 g VARNISH G (STEP I OF TABLE 11)

75 g STANNOUS OCTOATE

75 g ZINC OCTOATE

150 g TITANATE/ ZINC OCTOATE REACTION PRODUCT OF USP 3,196,166

150 g TITANATE EPOXIDE 206

25 g SOLUTION OF 10.8 g CATECHOL AND 139.2 g TURPENTINE AS  
ANTISKINNING AGENT

THE VARNISH WAS HEATED ON THE HOTPLATE TO 45 C AND STIRRED TO COOL.

c) INTRODUCING CHLOROSULFONATED POLYETHYLENE INTO EXPERIMENTAL COATINGS

THIS ELASTOMER IS KNOWN AS HYPALON 30 ( DU PONT, ELASTOMER CHEMICALS)

IT WAS CROSSLINKED HERE IN THESE VEHICLES BY COMBINATION WITH

A PHENOLIC RESIN AND TUNGOIL.

EXAMPLES : CODE V-3- 62.

VEHICLE : THE HYPALON ELASTOMER WERE DISPERSED IN BENZENE ( 25% HYPALON)

THE PHENOLIC RESIN WAS OBTAINED FROM THE DOLPH COMPANY, MONMOUTH JUNCTION,  
N.J.)

EITHER AS VARNISH AC-8 WHICH IS A N 8-8-8-VARNISH OF PHENOLIC

RESIN, TUNGOIL AND BODIED LINSEED OIL.

OR AS VARNISH AC 24 ,... A HEATED PHENOLIC VARNISH WITH TUNGOIL

ACCORDING TO THE SPECIFICATION MIX-V-1137-A

THE VEHICLE WAS OBTAINED FROM 60 g VARNISH AC -8 OR AC 24

100 g HYPALON-30 IN BENZENE 25%

6 g CATECHOL SOLUTION AS ABOVE.

THE PIGMENT PASTE WAS PREPARED BY BALLMILLING :

CONTINUED IN TABLE 14

FORMULATIONS USED IN THE PRESENT PERIOD (VII )

TABLE 14

TOPCOATS USED IN THE PRESENT PERIOD

c) INTRODUCING CHLOROSULFONATED POLYETHYLENE INTO EXPERIMENTAL COATINGS

V-3-62 ( CONTINUED FROM TABLE 13 )

THE PIGMENT PASTE BALLMILLED WITH:

- 100 g ACTIVATED CARBON H-21-71 HC
- 50 g SYNTHETIC IRON OXIDE :MAPICO RED #347
- 150 g 2 NITROPROPANE
- 40 g ALKYD RESIN AROPLAZ 1266- M 70

THE WHOLE PASTE WAS DILUTED WITH THE WHOLE VARNISH LISTED AT THE  
END OF TABLE 13

TO ACCELERATE THE DRYING A VERY SMALL AMOUNT OF THE SAME ACCELERATORS  
CAN BE ADDED AS USED IN SYNTHETIC RUBBERS SUCH AS TETRA METHYL THIURAM  
MONOSULFIDE ("UNADS") OR BENZOTHIOSYL DISULFIDE ("ALTAX")

THE SAME ACCELERATOR USED IN COMMERCIAL NEOPRENE PAINTS, SUCH AS  
GATES N-39 CAN HERE BE USED.

d) ANOTHER FORM OF ELASTOMER COATING ( CODE V-3-72)

- A) THE PHENOLIC VARNISH DOLPH AC-24 ..... 50 g IS  
DILUTED WITH METHYL ETHYL KETONE..... 20 g
- B) THE 25% HYPALON-30 SOLUTION IN BENZENE ....100 g IS  
DILUTED WITH METHYL ETHYL KETONE ..... 20 g
- C) A DISPERSION IS MADE FROM  
RUTILE TITANIUM DIOXIDE ..... 100 g AND  
DEHYDRATED CASTOR OIL (CASTUNG 103).. 50 g AND  
METHYL ETHYL KETONE ..... 20 g

THE SOLUTIONS A) AND B) ARE MIXED AND DILUTED WITH 20 g METHYL ETHYL KETONE  
THE DISPERSION C IS ADDED AND THE MIXTURE BALLMILLED.

THE PAINT IS USED OVER RED LEAD VINYL PRIMER.

with a carbon black, when the paints were compared under saltwater and supersonic vibration.

Again another approach to the same problem used phenolic varnish as well as the HYPALON solution further diluted with methyl ethyl ketone as the solvent. The pigmentation was here rutile titanium dioxide with dehydrated castor oil as vehicle and with methyl ethyl ketone as a diluent. The combination of these components was further diluted with methyl ethyl ketone and was ball-milled and applied. It was discussed in PART I that a strong transducer facing one of the highly polymerized coating systems can have a piercing effect on the very hard coatings. The resulting pattern of supersonic vibration attack appears as cavities, and this is to be avoided by increasing the coherence within the cross-linked systems.

For this aim TABLE 15 gives an example of an incorporation of a plasticizer of low volatility into a system of similar type as that shown in TABLE 13 c). As plasticizer here tricresylphosphate is incorporated into the paint paste.

A basically new approach is taken up in TABLE 16, where a plasticizer is not used but where two different elastomers are used in a paint of the elastomer type of TABLE 13- c with each of the elastomers being in a different state of polymerization. The very low polymer one of the two is chemically of a different kind from the high polymer one, and is of a type which progresses slowly into a highly cross-linked kind. Here the chlorosulfonated polyethylene (HYPALON-30) is combined in a ratio of 1:1 with a low molecular co-polymer of butadiene and acrylonitrile (HYCAR-1312). The cross-linking type phenolic resin-tungoil varnish component is maintained.

TABLE 17 shows the increased coherence of this paint by comparison with the straight HYPALON type paint, comparing the impact tests and the Taber Abraser pattern after 400 revolutions. In exposure in 5% saltwater under supersonic vibration the panels were in good state after 423 hours exposure.

FORMULATIONS USED IN THE PRESENT PERIOD (VIII )

TABLE 15

TOPCOATS USED IN THE PRESENT PERIOD

NEW APPROACHES IN MAINTAINING HIGHER COHESION IN THE NEW HIGHLY  
CROSSLINKED COATINGS

I) USING A SMALL ADDITION OF TRICRESYL PHOSPHATE IN A PAINT, SIMILAR TO V-3-62

(TABLE 13 - c, CONTINUED IN TABLE 14)

CODE V -3-81

PREPARATION PART A: 100 g ACTIVATED CARBON H-21-71 HC  
50 g SYNTHETIC IRON OXIDE (MAPICO RED # 347)  
150 g 2 NITROPROPANE  
40 g ALKYD SOLUTION AROPLAZ 1266 M 70 (CONTAINING  
28 g. ALKYD RESIN)  
10 g TRICRESYLPHOSPHATE

AFTER BALL MILLING:

PART B : 60 g PHENOLIC RESIN/TUNGOIL VARNISH (DOLPH AC 24 )  
ACC. MIL -V- 1137 A)

100 g CHLOROSULFONATED POLYETHYLENE SOLUTION 25% IN  
BENZENE (HYPALON 30)

10 g SOLUTION OF 10.8 g GATECHOL IN 139.2 g TURPEN-  
TINE (AS ANTISKINNING AGENT)

ADDITION OF SMALL AMOUNT OF ACCELERATOR FOR THE HYPALON COMPONENT

EITHER BENZOTHAZYL DISULFIDE (ALTAX) OR GATES ACCELERATOR N 39

THIS PAINT WAS APPLIED TO THE SAME WIREBRUSHED, PICKLING PROCEDURE,  
WASH PRIMER AND TWO COATS RED LEAD VINYL PRIMER AS THE CORRESPONDING  
PAINT WITHOUT TRICRESYL PHOSPHATE.

AFTER 125 HOURS EXPOSURE IN 5% SALTWATER UNDER ULTRASONIC VIBRATION THIS  
PAINT SHOWED NO CHANGES IN APPEARANCE AND PROPERTIES.

FORMULATIONS USED IN THE PRESENT PERIOD (IX.)

TABLE 16

TOPCOATS USED IN THE PRESENT PERIOD

NEW APPROACHES IN MAINTAINING HIGHER COHESION IN THE NEW HIGHLY  
CROSS-LINKED COATINGS (CONTINUED )

II. USING A LOW POLYMER, WELL SOLUBLE SYNTHETIC RUBBER AS MEDIUM OF INCREASING  
THE COHERENCE IN THE PAINT FILM:

USING A COMBINATION OF

CHLOROSULFONATED POLYETHYLENE ( HYPALON 30) (DU PONT DE NEMOURS)

A LOW MOLECULAR COPOLYMER OF

BUTADIENE AND ACRYLONITRILE

( Hycar 1312 LIQUID RUBBER  
GOODRICH CO.)

WITH A MEDIUM HIGH ACRYLONITRILE CONTENT

PART A: NITROPROPANE .... 150 g

ACTIVATED CARBON ..100 g

SYNTHETIC IRON OXIDE: 50 g

ALKYD RESIN SOLUTION:

AROPLAZ 1277 M 70: 40 g

PART II

PHENOLIC RESIN/TUNGOIL/  
LINSEED OIL VARNISH

AC 8 ..... 60 g

CHLOROSULFONATED POLY-  
ETHYLENE 25% IN: 50 g  
BENZENE (HYPALON 30)

LIQUID RUBBER(Hycar  
1312 ) 50 g

PLUS SMALL AMOUNT OF RUBBER ACCELERATOR (ALTAX OR GATES N 39)

CONTINUED IN TABLE 17)

FORMULATIONS USED IN THE PRESENT PERIOD ( X. )

TABLE 17.

TOPCOATS USED IN THE PRESENT PERIOD

NEW APPROACHES IN MAINTAINING HIGHER COHESION IN THE NEW HIGHLY  
CROSS LINKED COATINGS ( AGAIN CONTINUED )

II. CONTINUED:

ESTABLISHING THE DIFFERENCE IN THE PAINT COHESION WITHOUT AND WITH  
LIQUID RUBBER :

a) GARDNER IMPACT TESTER:

FALL WEIGHT FROM 20 in:

PAINT OF TABLE 13 C/14: ( V 3-62) WITH 100 g HYPALON 30-25% IN BENZENE

SHOWING IN THE FALL DENT CRACKING DOWN TO RED LEAD

PRIMER

PAINT WITH 50 g HYPALON-30 AND 50 g HYPAR 1312:

SHOWS NO CRACKING AT ALL

FALL WEIGHT FROM 28 in: SHOW SOME CRACKING ON BOTH.

b) CONICAL MANDREL TEST:

BENT 135 DEGREES : NO CRACKING ON ANY DIAMETER TESTED

c) SWARD HARDNESS TESTER :

PAINT WITHOUT HYPAR: AFTER 400 REVOLUTIONS EXPOSES THE RED LEAD VINYL

PRIMER ON ABOUT HALF THE TEST CIRCLE.

PAINT WITH HALF HYPALON SOLUTION

AND HALF HYPAR 1312 : AFTER 400 REVOLUTIONS: RED LEAD VINYL

PRIMER EXPOSED ONLY ON ABOUT 1 / 5 OF THE CIRCLE

d) WHEN THE NEW HYPALON/HYPAR PAINT OF TABLE 16 IS EXPOSED IN 5% SALTWATER UNDER

SUPERSONIC VIBRATION NO FAILURE IS OBSERVED AFTER

4 2 3 H O U R S E X P O S U R E

In TABLE 18 the low molecular weight HYCAR 1312 is used without HYPALON-30. The coatings were in good condition in the saltwater/vibration test after 305 hours, but showed afterwards under the GARDNER Impact Tester (fall from 28 inches) cracking at the point of impact.

Finally, in TABLE 19 a completely elastomeric experimental paint is being introduced, using 12.5 parts HYPALON-30 solids with 15 parts HYCAR-1312, and using in the curing the same factor as generally used in synthetic rubber; but this paint as formulated in Table 19 is a real paint. It can be applied as a paint to wire-brushed, wash-primer coated panels with red lead vinyl primer, and after application the paint dries. It is possible to increase the rate of hardening by 30 minutes exposure to 90°C.; but the paint dries without heat exposure. The rubber-type application of a similar formulation would require curing at about 310°F. (154°C.). This new type of elastomer paint is still to be studied further.

FORMULATIONS USED IN THE PRESENT PERIOD ( XI. )

TABLE 18

TOPCOATS USED IN THE PRESENT PERIOD

NEW APPROACHES IN MAINTAINING HIGHER COHESION IN THE NEW HIGHLY  
CROSS LINKED COATINGS

III. A COATING USING THE LIQUID RUBBER WITHOUT THE HYPALON 30

CODE V 3- 97

- A) NITROPROPANE... ..... 150 g  
ACTIVATED CARBON ..... 100 g  
SYNTHETIC IRON OXIDE  
MAPICO RED #347)..... 50 g  
ALKYD RESIN AROPLAZ  
1266 M 70 ..... 40 g
- B) PHENOLIC RESIN/TUNGOIL/  
BODIED LINSEED OIL  
VARNISH DC 8 ..... 60 g  
LOW MOLECULAR COPOLYMER OF  
BUTADIENE/ACRYLONITRILE 100 g  
OTHER ELASTOMERS ..... 0

PLUS ALTAX ACCELERATOR

ON PANEL: WIREBRUSHED

WASH PRIMER

2 COATS RED LEAD VINYL PRIMER

2 COATS ABOVE PAINT V 3-97

IN 5% SALTWATER UNDER SUPERSONIC VIBRATION AFTER

3 0 5 HOURS NO CHANGE IN CHARACTERISTICS.



## V. CONCLUSION- THE PRESENT STATUS OF THE DEVELOPMENT.

At this time we feel that the base treatment is in good condition.

It consists of the following aspects:

a) Removal of all oxidized and corroded layers, creating a newly exposed surface, by wire brushing or by sand / grit blasting.

b) Chemically reacting all parts of the surface, including the cavities of the surface profile, by the application of a chemical treatment of low viscosity which will not have difficulty in penetrating the cavities. This can be done, for instance, by some selected form of a pickling solution. In order to increase the penetration in the cavities, the driving out of air from the cavities, and the degree of chemical reaction with the steel, it is recommendable to utilize the solution at an elevated temperature. In the laboratory, and on smaller parts in the shop, this can be done by hot spraying of the pickling solution. The reaction surface is then to be allowed to dry before the next treatment is applied.

At this stage the surface is uniformly chemically reacted and reactive for further reactive coating applications.

c) Application of a primer coat of low viscosity, such as the wash-primer, or one of its modifications. This coat will penetrate into the cavities and chemically react with the earlier treatment. With the application of this primer coat, the metal substrate is freed from unreacted areas within the surface, which would present a starting point of corrosion as well as loss of adhesion.

It is to be mentioned that in our experience the specification wash-primer is not the only successful reactive, low-viscous primer. Many others are known to us and can be developed further for ship application.

d) It is necessary to form a uniform primer coat all over the surface which can represent the base for the top coat system. Hereby, the viscosity of the primer material can be increased gradually. That means when, for instance, two coats of a

primer are being applied, it is possible to apply the first one in a somewhat more diluted form than the second coat. The purpose is to give the first coat a better flow into the prepared and chemically pre-reacted cavities. It would be the ideal state when these cavities could be brought to where they no longer represent a separate factor. The second primer coat can then completely cover the whole system and represent the base for the top coat system.

Since we are trying here to produce a solid foundation and an adhesion base for the whole system, it appears recommendable that this primer should also be based on a reactive pigment. For example, we used red lead vinyl primer or zinc chromate vinyl primer or one coat of each. That here a reaction with the earlier treatment still can take place at all - as seen in the still increasing stripping weight - indicates that the wash primer coat alone did not fully eliminate the reactivity of the substrate. The last primer coat should no longer be able to produce an increase because it should no longer be in contact with the steel surface itself.

But since these more viscous primers also show an increased tendency to retain solvents, they produce the most solid base for the subsequent coatings when a short application of an elevated temperature could be provided. For smaller parts this does not represent a difficulty. For the outside of the ship it is still to be studied whether or not a short hot air blast might accomplish the desired effect.

After the primer layers are properly applied and dried, the ground foundation for any coating system is completed; and it is our feeling from our tests that afterwards the adhesion under supersonic vibration should not cause any special difficulties.

#### THE TOP COATS.

When some ten or fifteen years ago the vinyl system replaced more and more the earlier oleoresinous and alkyd systems, it was generally assumed that their main

feature is based on the characteristics of the particular type of polyvinyl resin used in a coating. And there is without doubt some merit to this approach. But the main basis for this success of the vinyl system over the earlier system is in another fact: In any of the earlier systems, the coating material contained very small amounts of pre-polymerized matter. In oil based coatings the content was minute. Then, in oil modified alkyds the per cent of initial polymer phase was somewhat higher, but the further progress of the polymerization in the applied coating was still slow; and the hardening of the coating itself and the resistance against saltwater were still limited. When the vinyl system came, it was the first system where a pre-polymerized resin was used in solution; and upon evaporation of the solvent, therefore, a film was obtained which had a considerably higher ratio of polymer matter than in the earlier coatings. But, here, still the final cross-linking or insolubilization and formation of a dense polymer film progressed very slowly. That is why the final coat with a combined vinyl and alkyd paint showed a considerably denser coating. We have worked on this system some years ago and there can be no doubt that this vinyl alkyd paint represented at that time the most highly cross-linked and densest coating which has been available. But still there was the fact to be faced that the alkyd component was not alkali resistant, and under exposure to the electrical effect of cathodic protection, it failed gradually on ship surfaces which were under cathodic protection.

The further development therefore must :

- a) continue to aim for highly polymerized coatings, or for coatings which after application continue to be cross-linked into the densest possible form without being saponified under cathodic protection.
- b) aim to include pre-polymerized materials for the group referred to as elastomers in connection with additives which will allow further cross-linking the applied elastomer.

How far did we get with these two problems? This project director faced the

problem of introducing polymer matter into oleaginous vehicles before their application some years ago. It was found that it is possible to air-blow oil at elevated temperature to gelation, that is, to such a high state of polymer content that the oil becomes insoluble, strongly swelling, and, at room temperature, strongly coherent, even extensible, like a rubbery compound. By continuing heating these gels with a metalsoap compound, the gels disperse into a fluid appearance, where they can be further dispersed with solvents in a varnish-like form. They maintain their viscosity in this form for years, but they still contain a high percentage of polymer matter. When these pre-gelled oils are applied, they are high in polymer content from the application on, and they can continue to harden by a combination of further polymerization and of surface oxidation of their applied coatings. In this form the coatings are highly coherent and resistant to seawater even under an electric current. This offered one possible approach.

The project director had observed also that metalorganic fluids can be produced based on one or more different metal components. These metalorganic compounds can be produced under vacuum distillation, whereby they are freed from low-temperature-volatile components and distill at about 2 mm. Hg. pressure at 280° - 300° Centigrade. These highly stable compounds can be cross-linked further with a metalorganic epoxide and turn into high-temperature-stable resins, which can be redispersed and introduced into coatings. They can be combined also with pre-gelled oil, as described above.

Combining these new components under pigmentation, etc., the first of our experimental paints has been obtained. Its drying can further be modified by a joint short heat exposure of these paints with a titanate epoxide, whereby the gel matter is increased. These paints turn into a dense polymer form and are stable under saltwater and under supersonic vibration. Only at a later stage of the past year, it was observed from exposure to a strong transducer at the Applied Science Laboratory in Brooklyn, that we had reached such a high degree of cross-linkage that the direct

bombardment with the ultrasonic energy caused a glass-like piercing in the center points of the radiation. There was no adhesion failure of any kind in the cavitation area; but we have discussed already how this coherence resistance against this energy can be increased.

A different form of new paint development this year referred to a combination of progressively cross-linking resinous vehicles with an elastomer which represents a chlorosulfonated polyethylene (Hypalon 30) which has a greater solubility than other elastomers such as are classified as synthetic rubbers, in particular much higher solubility than neoprene. The experimental paints which we have prepared some months ago on this basis were based either on a pigmentation of an alkyd solution or of a pre-gelled oil and by then introducing a 25% dispersion of the polyethylene derivative and further cross-linking the whole material by the introduction of a phenolic resin-tung oil varnish. Under the addition of a very small amount of any one of the common "accelerators" for synthetic rubber, the whole applied coating could be cured readily and was resistant against salt water and against supersonic vibration. Here again only the direct exposure to the strong energy emission of the transducer at the U. S. Naval Applied Science Laboratory in Brooklyn showed us that we might have gone too far in the cross-linking, since the factor of the energy bombardment caused here some piercing phenomena also. No failure of adhesion took place to any extent.

We are working, therefore, at this time to extend the coherence in these high polymer coating systems, which have not shown adhesion difficulties. It might appear possible to increase the coherence by less extensively pursuing the cross-linkage of the paint materials. This again, however, might cause speedy loss of adhesion such as occurred at the start of the project; or, when a gradual effective cross-linking would take place after paint application, it might result in gradual loss of coherence, which is not desirable. Therefore, a new experimental coating

might be developed where a new component is introduced into the coatings which have been developed in this report, with this new component having the properties (a) of not gelling at all without interfering with the progress of the gelation of the coating itself, and (b) gelling under such different conditions that its own gelling would not take place during the curing of the experimental paint. Some exploratory tests have been made with respect to using non gelling additives, such as by incorporating some form of "plasticizer" such as tricresyl phosphate. Such a combination with the experimental paints of this project have stood up well under saltwater exposure with supersonic vibration.

A new, different approach to the problem of obtaining good adhesion as well as good coherence in an elastomeric paint was made with exploratory tests introducing a synthetic rubber in a low-polymer, still-fluid form into a dispersion of a highly cross-linked form of another synthetic elastomer. In this case a liquid form of a butadiene-acrylonitrile rubber, having a medium high acrylonitrile content, was combined with a dispersion of the chlorosulfonated polyethylene, such as used in earlier tests of this report. That means, for instance, by weight one-half of the chlorosulfonated polyethylene (Hypalon 30) was replaced by liquid HYCAR 1312. This combination of two elastomers in widely different states of crosslinkage was incorporated in an experimental paint and showed during more than 400 hours exposure to 5% saltwater under supersonic vibration a very good stability. The coating stood up well under impact tests also, and did not show loss of adhesion when after the impact test the panels were returned to the saltwater exposure under vibration conditions.

Another new approach included the incorporation of rubber accelerators, or the crosslinking with titanate epoxide into elastomeric test paints. In the very last work on the exploratory tests the Hypalon type experimental test paints were modified further by omitting the phenolic resin-tungoil component. The paint was here used as a rubber-like paint compound based on the two different polymer state elastomers as just outlined above. Hereby, sulfur was introduced in the pigmented elastomer compound as a "vulcanizing" agent.

In applying the new elastomer type paints, the substrate was prepared in accordance with the recommendations outlined earlier, on pages 52-53 of this report. The tests under 5% saltwater and vibration conditions were very promising with these new types of elastomer coatings.

Basically, in comparing these new elastomer coatings of this project with the conventional commercial neoprene coatings, the difference is that a dispersion of neoprene necessarily produces a low elastomer concentration in the solution, therefore requiring a considerable number of coats in building up a coating system, and each coat has the tendency to retain solvent residues in the coating. The new coatings, on the other hand, have a high elastomer concentration since they contain partially an elastomer which can be dispersed in an approximate 30% solution. The other elastomer is for itself liquid . Therefore, they produce a heavier film thickness in fewer coats. These high elastomer paint coatings on steel can be expected to produce the required conditions in the dome area also, without requiring extensive structural modifications of this area.

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APPENDIX

a)

REFERENCES CITED

- (1) Kronstein, M., Carroad, M.R. and Byrd, J.J., "THE GELATION EFFECTS OF TETRA ALKYL TITANATES ON ELASTOMERIC COATING MATERIALS", in JOURNAL OF PAINT TECHNOLOGY-OFFICIAL DIGEST, Vol. 38, No. 492, pages 37-42 (January 1966).
- (2) Kronstein, M., Carroad, M. R. and Byrd, J. J., "THE GELATION EFFECT OF TETRA ALKYL TITANATES ON THE FORMATION OF POLYMER RESINS", in OFFICIAL DIGEST (of the Federation of Societies for Paint Technology), Vol. 37, No. 482, pages 284-301 (March 1965) .
- (3) Kronstein, M. , "Solubilizing Insoluble Gelatinized Oils", U.S.Patent 2 476 879, July 19, 1949.
- (4) Kronstein, M. "Solubilizing at least Partially Insoluble and Gelatinous Waxes and Oils", U. S. Patent 2 568 550 and 551 , September 18, 1951.
- (5) Kronstein, M., "Stable Dispersions of Oil Gels", in PAINT AND VARNISH PRODUCTION magazine, Vol. 50, No. 4 (April 1960).
- (6) Kronstein, M. and Kapfer, W.H., "Complex Alkyl Titanate Derivatives" , U. S. Patent 3 196 166, July 20, 1965.
- (7) Kronstein, M., Von Burgsdorff, W. A., Hanan, N. and Weir, D. L., "Utilizing Molybdenum Compounds in the Surface Protection of Steel", in pre-print book "Papers Presented at the Atlantic City Meeting", of the American Chemical Society, Division of Organic Coatings and Plastics Chemistry, Vol. 25, No. 2, pages 173-191, (September 1965).

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b)

SPECIFICATION PAINT MATERIALS USED IN THE PROJECT

TT-R-266 a, RESIN ALKYD, SOLUTION, TYPE 1:LONG OIL SOYA-MODIFIED.

MIL-V-1137 A, VARNISH, ELECTRICAL, INSULATING.

MIL-P-15328B (FORMULA 117) PRIMER, PRE-TREATMENT FOR METALS ( WASH-PRIMER).

MIL-P-15929B (FORMULA 119) PRIMER COATING, SHIPBOARD, VINYL-RED LEAD.

MIL-P-15930B (FORMULA 120) PRIMER, VINYL-ZINC CHROMATE TYPE.

MIL-P-15931B (FORMULA 121/63) PAINT ANTIFOULING, VINYL, RED.

MIL-E-15936B (FORMULA 122-27) ENAMEL EXTERIOR GRAY, VINYL-ALKYD

MIL-P-22299 (SHIPS) (FORMULA 134) PAINT ANTIFOULING, POLYISOBUTYLENE.

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APPENDIX (CONTINUED).

c) PROPRIETARY MATERIALS

The commercial materials listed below have been used in the work of this project:

ACTIVATED CARBON H-21-71-h UNION CARBIDE CHEMICALS CO.

ALTAX RUBBER ACCELERATOR (Benzothiazyl disulfide) R.T.VANDERBILT CO., Inc.

ALUMINUM 5 XD REYNOLDS METALS COMPANY, PIGMENT DIVISION.

AROPLAZ 1266 M 70 (Long oil soyabean modified according to TT-R-266 a) ARCHER-  
DANIELS-MIDLAND

CARBON BLACK SRF FUMEX COLUMBIAN CARBON CO.

CASTUNG-103 (Dehydrated castor oil) BAKER CASTOR OIL COMPANY

EPOXIDE-206 (Vinyl cyclohexene dioxide) UNION CARBON CHEMICALS CO.

EPONOL 55 RESIN SHELL CHEMICAL CORPORATION  
HYCAR 1312 (Liquid Rubber) (Low molecular copolymer of butadiene and acrylonitrile)  
THE B. F. GOODRICH CHEMICAL CO.

HYPALON 30 (Chlorosulfonated polyethylene) E. I. DU PONT DE NEMOURS & CO., ELASTOMER  
CHEMICALS.

MAPICO RED ( synthetic iron oxides) COLUMBIAN CARBON CO.

N-39 COLD BOND (Commercial neoprene paint) GATES ENGINEERING COMPANY

PHENOLIC RESIN VARNISH SYNTHITE AC-8 and AC-24 ( clear air drying varnishes)  
according to MIL-V-1137 A. JOHN C DOLPH COMPANY.

UNADS ACCELERATOR (Tetra methyl thiuram monosulfide) R.T.VANDERBILT CO, INC.

ZINC OCTOATE, BASIC: SILICURE Z-775 NUODEX PRODUCTS DIVISION OF HEYDEN NEWPORT  
CHEMICAL CORPORATION.

ZINC DUST #22. NEW JERSEY ZINC COMPANY.

d) COMMERCIAL EQUIPMENT USED

Brush Surface Analyzer, Model BL-103. BRUSH ELECTRONICS CO., CLEVELAND, OHIO.

SONOGEN LGTH-40 (Ultrasonic generator & tank) Branson Instruments, Inc., Stamford, Conn.

SONIFIER MODEL S-125. HEAT SYSTEMS COMPANY, Melville, L.I., N.Y.

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