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# The Development of a Nontoxic Self-Extinguishing Paint for the Interior of Nuclear-Powered Submarines

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## ABSTRACT

Efforts have been made to develop a high-quality interior paint for nuclear-powered submarines. Because of the circumstances under which the paint is to be used, it must have properties not previously required for ships in the fleet. It should (a) release little or no toxic or organic material to the atmosphere as it is applied or as it dries, (b) be self-extinguishing in its fire-retardancy performance, (c) have a gloss in the medium range (50% at a 60° angle), (d) be flexible, and (e) have a highly decorative appearance in general.

Chlorinated compounds and antimony oxide were used to introduce fire retardancy into an acrylic latex paint; however, they also affected the physical appearance and performance of the paint. The highest degree of fire retardancy and best overall properties were obtained when a chlorinated paraffin and antimony oxide were used together. The tentative concentrations have been selected as 34 wt-% for chlorine and 14 wt-% for antimony oxide, based on the weight of nonvolatile, combustible material in the paint. Further changes are being made in this formulation to improve performance.

A film-forming polymer which contains chlorine chemically combined with the polymer was studied, and a formulation was devised making use of this material. It is also undergoing further examination.

## PROBLEM STATUS

This is an interim report; work continuing on this problem.

## AUTHORIZATION

NRL Problem C08-18  
Project SF 013-08-03-4095

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## THE DEVELOPMENT OF A NONTOXIC SELF-EXTINGUISHING PAINT FOR THE INTERIOR OF NUCLEAR-POWERED SUBMARINES

### INTRODUCTION

Paints used in the interior of nuclear-powered submarines must have a special combination of properties not previously required for the ships in the fleet (1a). These properties can be readily incorporated into a conventional solvent-base paint; but since the atmosphere in a nuclear submarine must be rigorously controlled (1b), painting with these organic solvent-thinned paints must be stopped five days before the submarine departs to sea (2). However, it is not always possible to meet this schedule, since it is desirable, and many times necessary, to delay most of the interior painting until the other maintenance work is completed. During this five-day period, a paint must be used which does not release toxic materials as it is applied and dries. Three commercially available latex paints have been approved for use during this period (2). However, each of these paints lacks certain performance characteristics, making them undesirable for widespread use. Therefore, a program has been initiated to develop a high-quality paint for use during this interval and even under sealed-ship conditions.

### DEFINITION OF PROBLEM

In addition to being nontoxic, this paint must also be fire retardant. Ideally, the paint film should be self-extinguishing when the source of ignition is removed. Since these paints will be applied only to steel structures or nonburning, flexible insulation, the ability of the paint to protect a combustible substrate is of little or no interest. The fire-retardant requirement of the paint would be to prevent the possibility of a localized fire spreading to other areas by way of a burning paint film. Otherwise, this hazard would become critical with the increased number of paint layers accumulated over the years.

As a third requirement, the paint film must also be flexible when dried. Approximately 60,000 sq ft of flexible insulation is used in the interior of today's nuclear submarines. Until recently, the solvent-base chlorinated alkyd, Formula 124/58 (3), was used to paint this material. However, because this paint dries to a brittle and nonflexible film and severely cracks on the flexible insulation, instructions had to be changed to permit the use of only flexible coatings described in Ref. 4. Thus, any newly developed paint should be suitable for use on resilient materials.

A fourth requirement is that the paint should have a minimum gloss equivalent to the chlorinated alkyd formulation 124/58 which it is to replace. This should be between 35 and 50%. Preferably, the gloss should be above 50%. A paint with a good gloss is desirable because of its greater resistance to soilage as well as its more decorative or esthetic value.

The introduction of these four properties, nontoxicity, fire retardancy, flexibility, and medium gloss, should not cause deterioration in other paint properties. An acceptable paint must also have sufficient hiding power to cover an area in two coats, and preferably, one coat. Leveling must be sufficient to yield a reasonably smooth surface which does not show brush marks. Poor leveling will be more noticeable and therefore more objectionable with medium gloss paints than with flat paints. It should be capable of withstanding

the same abuse of moisture, abrasion, oil and grease, temperature, etc., as is the chlorinated alkyd. Finally, having achieved these properties in the paint, it must still perform its primary function of protecting the structural materials from corrosion and deterioration.

#### EARLIER WORK

Because of the widespread habit of interior painting on patrols and the lack of success in discouraging this practice, the Bureau of Ships in 1958 requested the U.S. Naval Research Laboratory to develop a "touch-up paint" which could be used while the submarine was actually submerged. It was hoped that this action would develop specifications for an acceptable paint and thus eliminate or at least greatly reduce the practice of using supposedly safe, but untested paints. This work led to the development of a semigloss acrylic latex paint. Highly successful evaluation of this paint on the nuclear submarines TRITON (SSR(N)586), HALIBUT (SSG(N)587) and the THOMAS A. EDISON (SSB(N)610) has been reported (5-7). It should be emphasized that this paint was developed only for touch-up purposes for use when the chlorinated alkyd paint, Formula 124/58, could not be used because of its release of toxic vapors of organic solvents into the submarine's atmosphere. However, because of continuing difficulties in adhering to the paint schedule prescribed by Ref. 2, particularly in overhauling submarines, an alternative for the solvent-base paint was sought which would have at least the same minimum performance while not releasing toxic materials into the atmosphere.

The NRL acrylic formulation was nontoxic and equal or superior to Formula 124/58 in many of its performance characteristics, but it was not fire retardant. Although leveling and adhesion to oily or chalky surfaces were somewhat inferior to Formula 124/58, these properties were not so deficient as to prevent this formulation from being an excellent replacement. In short, the only major deficiency in the NRL acrylic paint is fire retardancy.

#### PRESENT STATUS

Currently three commercial water-base paints are approved for use (4) in lieu of Formula 124/58. Since all three are flexible, they can be used on resilient materials such as Ensolite.\* However, they are inferior to the chlorinated alkyd in a number of respects and therefore are not suitable for widespread use. In general, their gloss is poor, the best having a 60° gloss of 32%, hiding is marginal, and freeze-thaw stability is poor. In addition, a thick coating of one of the three approved types is not self-extinguishing and will continue to burn slowly after the source of ignition is removed. Another, although dry to touch, retains a surface tackiness for at least several weeks after application. Thus, at best, these commercial coatings represent only a stop-gap solution and should be used sparingly. The properties of these three commercial paints, the NRL acrylic, and Formula 124/58 are summarized in Table 1.

#### CURRENT WORK

##### Fire Retardancy

The evaluation of the flammability of any substance is a difficult, time-consuming, and generally inexact procedure. Although a completely self-extinguishing paint is desired, the effect of fire-retardant additives on the burning characteristics of a paint would provide guidelines for further modification. On the other hand, highly quantitative data would not be required, since small differences in flammability probably would not be a deciding factor in selecting a formulation when all the other performance characteristics are considered. It is hoped that a paint can be developed that is immediately self-extinguishing when the source of ignition is removed. Although undesirable, it might be necessary to

\*U.S. Rubber Company's trade name for the unicellular, elastomeric, poly(vinyl chloride) foam used for insulation and shock absorption, MIL-P-15280D, Apr. 3, 1962.

Table 1  
Properties of Interior Paints for Nuclear Submarines

Properties	Formula 124/58	NRL Acrylic	Devflex MD-2707	Amercoat 88-S	Ocean 634
Hiding (qualitative)	Good	Good-Fair	Fair	Fair	Fair
60° gloss (Gardner)	55% (35-50%)*	58%	32%	23-32%	9%
Leveling (NYPC leveling test blade)	7 (Good)	5 (Fair)	7 (Good)	0 (Poor)	6 (Good)
Freeze-thaw stability (0° F to 72° F)	Stable	10 cycles	0 cycles	2 cycles	0 cycles
Flexibility on Ensolite	Poor, cracks	Good	Good	Good	Good
Water-scrub resistance† (cycles for film failure)	3700	4000	1450	850	1300
Fire retardancy of thick coating on asbestos paper	Immediately self-extinguishing	Burns completely	Burns approx. 6 in. before self-extinguishing	Burns completely	-
Fire retardancy of one coat on asbestos paper (10 mil wet film)	Immediately self-extinguishing	Burns completely	Self-extinguishes after approx. 1 sec of burning.	Self-extinguishes after approx. 1 sec of burning.	Immediately self-extinguishing
Fire retardancy of one coat on Ensolite	Nonburning	Burns	Nonburning	Nonburning	Nonburning
Toxicity	High	Low	Low	Low	Low

\*Specifications

†Gardner Model 105 straight line washability and abrasion machine. Abrasion medium contained 15 g 400-cps methocel, 10 g. Castile soap, and 30 g pumice powder in 1 kg water. Film surface scrubbed with hog-bristle brush.

compromise with other performance properties and requirements and use a paint which will burn for a few seconds before self-extinguishing.

A suitable testing procedure has been developed which will readily allow rating the flammability of the dry films with reasonable speed and precision, so that even differences in burning rates of completely combustible films can be measured.

In this test, a wet film 5-1/2 in. wide is laid down with a 10-mil Dow film caster on an 8 × 11 in. sheet of asbestos paper (Fisher Catalog No. 1-470) approximately 1/64 in. thick and held flat by a Bird vacuum plate.

The film is allowed to dry for at least five days and then the coated area is cut into five 1 × 11 in. test strips. The test strips are ruled off at 2, 3-1/2, and 9-1/2 in. from the bottom. Since these ruled lines may become covered with soot or smoke or otherwise made obscure during the test, it is convenient to punch a small hole in the test strips at these three locations to facilitate the identification of their position. The test is made in a cabinet whose interior dimensions are 19 × 13 × 33 in. It has a glass front door through which the burning sample can be observed. Along the bottom of both sides of the cabinet are several 1/2-in.-diameter holes for ventilation. The top of the box has two 1-in.-diameter holes diagonally opposite each other and one in the center over which a small exhaust fan is positioned to help remove the smoke formed during the test. The cabinet is in a hood which is kept on during the test to remove the combustion gases. With the cabinet door closed and the hood and small exhaust fan on, there is little or no flame disturbance caused by air currents. The 1 × 11 in. test strip is suspended vertically in the cabinet by any number of suitable means. One convenient method is to use two nails held in position by clamps on a 1/2-in.-diameter rod fastened to the top and bottom of the cabinet. The clamps are approximately 10 in. apart, and the asbestos strip is simply pushed onto the nails. To prevent the asbestos from tearing when tightening and aligning the test strip, a small piece of masking tape at the point of puncture is helpful. After the test strip has been positioned, a microburner is aligned with the test strip so that a line passing through the barrel of the burner is perpendicular to the strip at the center of the 2-in. mark and the tip of the barrel is 2 in. from the strip. The torch is lit with the air intake port closed so that a yellow flame is formed that burns straight up and does not reach the test strip. The cabinet door is closed and air intake of the burner fully opened by an external linkage. This causes a hot, blue flame which burns straight out and ignites the sample. The time for the paint film to ignite and burn from the 2-in. mark to the 3-1/2-in. mark, at which point the burner is extinguished, and from the 3-1/2-in. mark to the 9-1/2-in. mark is measured with two stopwatches. The time to burn the 1-1/2 in. is called the ignition time and is related to the ease of ignition of the paint. The time to burn the 6 in. after the torch has been extinguished is referred to as the burning time and is dependent on the fire retardancy of the coating.

Ideally, the coating would self-extinguish as soon as the microburner is turned off, and therefore would have an infinite burning time for the 6-in. length. However, depending on the degree of fire retardancy, it may continue to burn for a time before it self-extinguishes; or it may burn the whole 6-in. length at a rate proportional to its degree of fire retardancy. The sum of the ignition and the 6-in. burning time is called the total burning time. For those films which are completely burned, the total burning time appears to be the more useful and reproducible value in correlating the observed effects (data) with paint composition.

The graphs shown in Figs. 1 through 5 were prepared from the data obtained by this procedure. As previously discussed, the procedure for preparing a sample for evaluation gives five identical test strips; and therefore each point on the graphs is the average of five tests, except when some strips are self-extinguishing. When a strip is self-extinguishing, its ignition time is included in the ignition-time average, but its burning time (infinite) is not included. The number of self-extinguishing samples is reported as a fraction at the

top of the graph. Thus in Fig. 2, the average ignition time for the five test strips prepared from a formulation (paint) containing 12.5 wt-% chlorine was 9.4 sec. However, two of these test strips (2/5) failed to burn the 6 in. after the microburner was turned off. It is not important for this discussion whether these test strips are immediately self-extinguishing or continue to burn for a few inches (but less than 6 in.) before self-extinguishing. The 6-in. burning time and the total burning time for the example paint, containing 12.5 wt-% chlorine, is the average of only the three test strips which burned the full 6 in. after the microburner was turned off.

Generally, the fire-retardant additives had little or no effect on the ignition time as measured by this procedure. Their effect is much more pronounced on the 6-in. burning time and the number of self-extinguishing samples. Throughout the subsequent discussion of these experiments, attention will be focused primarily on the number of self-extinguishing samples and total burning time because of the minor effects observed for ignition.

As stated before, this test was not developed to give highly quantitative data but to provide a fairly rapid screening for numerous formulations that were to be studied. There are a number of variables that are ignored, such as variations in moisture content of the asbestos, small differences in coating thicknesses, variations in the microburner flame temperature caused by variation in gas composition and pressure, and others. Nevertheless, once minor problems were worked out and a standard procedure developed, data were quite reproducible, and the test seems well suited to our needs.

The thickness of the dried paint film has a marked effect on the burning time, and the success of obtaining reproducible data is dependent on comparing films of the same thickness. Figure 1 shows data for the NRL acrylic paint of various film thicknesses. The dry film thickness was measured with a micrometer. The wet film thicknesses (film caster clearance) are shown in parentheses above the dry film thicknesses.

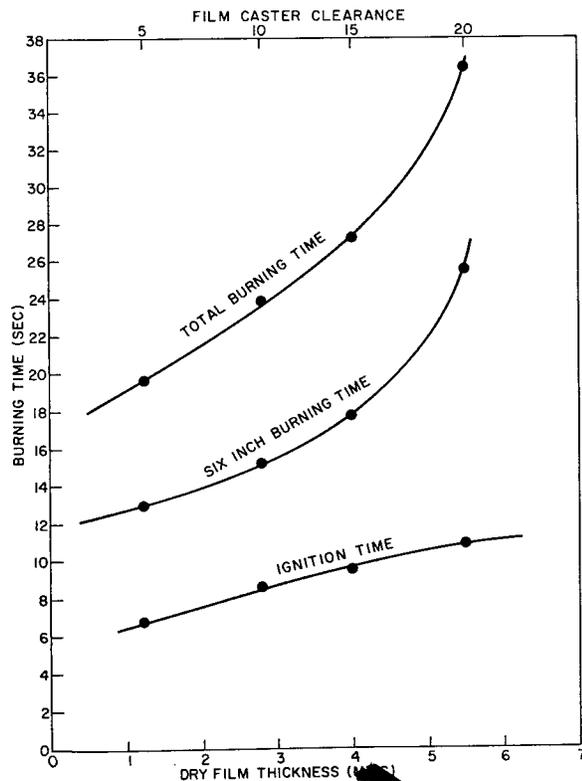


Fig. 1 - Relationship between dry film thickness and burning time, for NRL acrylic prepared by Sherwin-Williams

As can be seen in Fig. 1, the burning time increases as the film thickness increases. The inference would be that the fire retardancy of the paint improves as the film thickness increases. Actually, the flammability of the paint is not affected; but since more of it is present, it will take longer to burn. Thus a problem arises in interpreting whether the change in burning time results from a change in the fire retardancy of the paint or from a change in film thickness. The two effects can be distinguished by observing the nature of the flame. Thus with a true increase in fire retardancy, the film will burn with a small and less intense flame, while the effect of increased film thickness will be a larger, brighter, and hotter flame.

Table 2 summarizes the test results for Formula 124/58 (the chlorinated alkyd), the NRL acrylic, and the three commercial fire-retardant latex paints. All but the NRL acrylic are supposedly fire-retardant paints.

#### Modification of NRL Acrylic Latex Paint

Because of the many desirable qualities of the NRL acrylic paint, such as gloss, scrub resistance, hiding power, and nontoxicity, initial efforts were toward introducing fire retardancy into this formulation. This has been accomplished by addition of a chlorinated paraffin, Unichlor 70B, and antimony oxide to the basic NRL formulation as shown in Table 3. A change in the thickening agent was also made in an unsuccessful attempt to improve the leveling of the paint. The antimony oxide was proportionally substituted for a small part of the titanium dioxide, and thus the total pigment weight was unchanged. However, the chlorinated paraffin was added to the formulation with no change in the weight of the acrylic resin or other ingredients. It remains to be determined whether the chlorinated paraffin coalesces with the acrylic resin and thus should be considered as part of the vehicle or remains as discrete particles which might be considered to bulk in the film similarly to an extender pigment. This point will be discussed later.

Because of the adverse effect of the fire-retardant additives on paint properties and performance, it was desirable to know how much chlorine, in the presence of antimony oxide, would be necessary to render such a formulation self-extinguishing. Therefore, a series of formulations were prepared in which the Unichlor content was varied from 0 to 26.9 wt-% in the dried paint film. Since the Unichlor contains 70 wt-% chlorine, the actual chlorine content varied from 0 to 18.8 wt-%. The composition of these formulations is summarized in Table 4. The volatile components (water, carbitol, etc.) are not shown. Since the chlorinated paraffin does not burn, it was not considered as part of the combustible solids. The combustible solids include only the acrylic resin and the small amounts of organic material from the defoamers, thickeners, surfactants, and grinding vehicle.

The manner in which to express the effect of the paint composition on the fire retardancy of the paint is somewhat of a problem. First, the paint ingredients may be expressed in terms of either the volume used or the weight used, as shown in Table 4. Generally, volume is used in relating paint properties to composition. However, in the case of fire retardancy, there appears no basic reason for expressing paint composition in volume units. Further, it would be difficult, if not impossible, to calculate the actual volume contribution of the chlorine from the chlorinated paraffin, while the weight contribution of chlorine is already known. It could also be argued that since the antimony oxide and chlorine interreact to give a synergistic effect the chemical reaction could be more easily described using moles of reactants calculated from weights rather than volumes. For these reasons, weight units are used to express the composition of the formulation.

The biggest problem, however, has been changes in more than one parameter as the chlorine content was varied. Essentially, the paint is composed of four basic materials: titanium dioxide, antimony oxide, the vehicle, and the chlorinated paraffin. To increase the chlorine content, more Unichlor is added to the formulation. If the pigment-to-organic



Table 3  
NRL Acrylic Formulation and Modified, Fire-Retardant Formulation\*

Ingredients	Function	Weight-% of Ingredients	
		NRL Acrylic	Modified Acrylic (Fire retardant)
<u>Premix</u>			
1. Titanium dioxide (R-100)	Pigment	24.70	17.76
2. Antimony oxide (KR grade)	Fire retardant pigment	-	3.27
3. Amberlac 165 (21%)	Grinding vehicle	4.41	3.76
4. Triton CF 10	Surfactant	0.18	0.15
5. Tamol 731 (25%)	Surfactant	0.72	0.60
6. Nopco 1407	Antifoam	0.18	0.15
7. G-11 (hexachlorophene)	Preservative	0.09	0.08
8. Unichlor 70B	Fire retardant	-	10.94
9. Water	Thinner	7.06	10.01
<u>Let Down</u>			
10. Rhoplex B60-A (45%)	Vehicle	31.76	27.04
11. Rhoplex C72 (45%)	Vehicle	22.94	19.54
12. Carbitol	Coalescing aid	4.41	3.76
13. Polyglycol P1200	Drying regulator	0.44	0.38
14. Pine Oil	Antifoam	0.44	0.38
15. Bubble Breaker	Antifoam	0.44	0.30
16. WSR-301 (4%)	Thickener	1.76	-
17. Polyvinylpyrrolidone (20%)	Thickener	0.48	-
18. Methocel HG 400 (4%)	Thickener	-	1.92

* Constants	NRL Acrylic	Modified Acrylic
Total solids	51.55%	54
Pigment volume content	20. %	16.3%
Viscosity	62 KU	-
Gloss (60°)	58 %	29 %
Wt-% Unichlor in nonvolatile solids	0	20.2%
Wt-% chlorine in nonvolatile solids	0	14.1%
Vol-% Unichlor in nonvolatile solids	0	21.0%
Vol-% antimony oxide in nonvolatile solids	0	1.96%

material ratio is to be kept constant, then an equivalent amount of vehicle must be removed. But since the vehicle is the only source of fuel (the Unichlor is nonburning), then not only does the chlorine content increase, but the fuel content decreases. Thus a change in fire retardancy results from both the increase in chlorine content and the decrease in fuel content. If Unichlor is considered as a pigment, it can be seen from Table 4 that if an equal weight of titanium dioxide is removed to keep the ratio of combustible (vehicle) material to noncombustible (titanium dioxide, antimony oxide, and Unichlor) material constant, then practically all the titanium dioxide would have to be replaced in formulation IV. Such a replacement would be expected to influence fire retardancy in addition to the effect caused by increasing the chlorine content. It would also be pointed out that if these replacements were made on a volume basis, removal of all the titanium dioxide and the antimony oxide from formulation IV would correct for only one half of the volume increase due to the addition of the Unichlor. The method we used, keeping the weight of titanium dioxide, antimony oxide, and vehicle constant and varying the amount of Unichlor, does not solve the problem either, since the ratio of combustible solids to total solids decreases as the chlorine content is increased. Again, one would expect this change in the ratio of combustible solids to total solids to affect the fire retardancy in addition to the effect of the chlorine content.

Table 4  
Nonvolatile Solids Composition of Formulations Used in Obtaining Data for Fig. 2

	Formulation I Parts By		Formulation II Parts By		Formulation III Parts By		Formulation IV Parts By	
	Wt.	Vol.	Wt.	Vol.	Wt.	Vol.	Wt.	Vol.
Titanium dioxide (R-100)	6.96	9.30	6.96	9.30	6.96	9.30	6.96	9.30
Antimony oxide (KR grade)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Vehicle*	8.43	41.17	8.43	41.17	8.43	41.17	8.43	41.17
Unichlor 70B (70% Cl)	0.00	0.00	1.51	4.98	3.02	9.96	6.07	20.02
Total	16.39	51.47	17.90	56.45	19.41	61.43	22.46	71.49
% solids in paint	51	-	53	-	55	-	56	-
Pigment content	-	20.0	-	18.2	-	16.8	-	14.4
% Unichlor in total solids†	0	0	8.4	8.82	15.6	16.2	27.0	28.0
% chlorine in total solids†	0	-	5.9	-	10.9	-	18.8	-
% antimony oxide in total solids†	6.1	1.94	5.6	1.77	5.2	1.63	4.5	1.40
% Unichlor of combustible solidst	0	0.00	17.9	12.1	35.8	24.2	72.0	48.7
% chlorine of combustible solidst	0	-	12.5	-	25.1	-	50.4	-
% antimony oxide of combustible solidst	11.9	2.43	11.9	2.43	11.9	2.43	11.9	2.43
% combustible solidst in total solidst	51.4	80.00	47.1	72.9	43.4	67.0	37.5	57.6

\*The vehicle includes acrylic resin, thickener solids, defoamer, grinding vehicle solids, etc.

†The total solids includes pigments, vehicle\*, and Unichlor.

‡The combustible solids includes only the vehicle\*.

In the series of formulations in Table 4, the percent combustible solids in the total solids varies from 51 wt-% in formulation I to 38 wt-% in formulation IV. Information as to the contribution of this change of 13 wt-% on fire retardancy is not available. The change may well be small enough that its effect on fire retardancy is minor in comparison with the change in chlorine content. If this small change in combustible solids can be neglected, then the only important variable is the chlorine content; the antimony oxide content remains constant at 11.9 wt-% of the combustible solids.

Under the conditions and interpretations discussed above, Fig. 2 shows the effect on fire retardancy of varying the chlorine content of an acrylic latex paint. As can be seen in the graph, the total burning time increases and the number of self-extinguishing samples increases as the chlorine content increases. The number of self-extinguishing samples is indicated at the top of the graph as a fraction. For example, at 12.5 wt-% chlorine, two out of five (2/5) samples self-extinguished. At some chlorine content between 25.5 and 50.5 wt-% of combustible solids all samples become completely self-extinguishing. All the samples containing 50.5 wt-% chlorine self-extinguished immediately after the micro-burner was turned off.

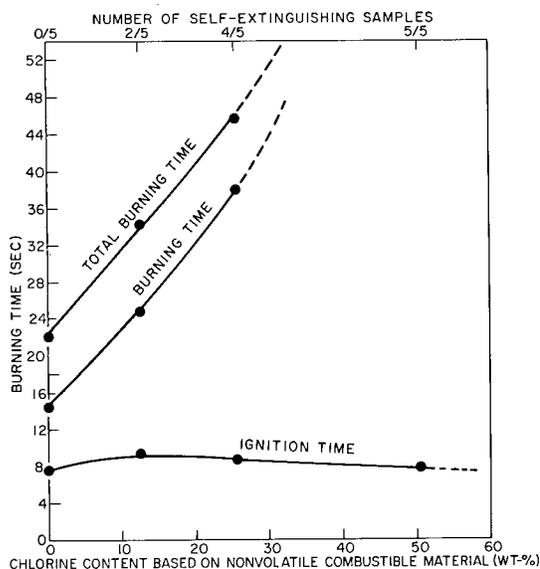


Fig. 2 - Effect of aliphatic chlorine content on fire retardancy, for an acrylic latex paint containing 12 wt-% antimony oxide based on nonvolatile combustible solids

For comparative purposes, the NRL acrylic, containing no chlorine or antimony oxide, was tested at the same time. Two series of five samples each were tested and the agreement between the two series was good: ignition times were 8.3 and 8.5 sec, burning times 14.8 and 13.1 sec, and total burning times 23.1 and 21.6 sec, with no self-extinguishing samples. It can be seen that there is no significant difference in fire retardancy between the NRL acrylic and the modified acrylic containing the 12 wt-% antimony oxide but no chlorine. Although at low concentration the antimony oxide in the absence of chlorine contributes little or no fire retardancy to the formulation, its effectiveness in the presence of chlorine is illustrated by comparing the fire retardancy of two formulations containing 25.5% chlorine, but one of which contains no antimony oxide and the other 11.9 wt-%. While four out of five samples were self-extinguishing with the samples containing the antimony oxide, none was self-extinguishing when the antimony oxide was replaced by an equal weight of titanium dioxide. The total burning time for the one antimony oxide sample which burned completely was 45.6 sec, while the average for the 5 samples containing no antimony oxide (but containing the same amount of chlorine) was only 26.0 sec.

The effect of antimony oxide on fire retardancy is better illustrated from the data presented in Fig. 3. In this series of formulations, the chlorine was held constant at 24.8 wt-% of the nonvolatile, combustible solids, and the combustible solids held constant at 43.6 wt-% in the total nonvolatile solids. The antimony oxide content was varied by replacing part of the titanium dioxide by an equal weight of antimony oxide. The NRL acrylic latex (no antimony oxide or chlorine; 52 wt-% combustible solids) was tested at the same time for comparative purposes; no samples self-extinguished and the total burning time was 22.5 sec. It can be seen that the 24.8 wt-% chlorine in the absence of antimony oxide (0 wt-% antimony oxide) does give a slight improvement in fire retardancy over the NRL acrylic which contains no chlorine. Although no samples self-extinguished, the total burning time was 26.1 sec compared with 22.5 sec for the NRL acrylic. With the addition of only 2.0 wt-% antimony oxide, based on the combustible solids weight, fire retardancy was greatly improved, with 3 out of 5 samples self-extinguishing when the microburner was turned off and with an increase in total burning time to 29.7 sec for the two samples that did burn completely. At 19.8 wt-% antimony oxide, all 5 samples self-extinguished immediately after the microburner was turned off.

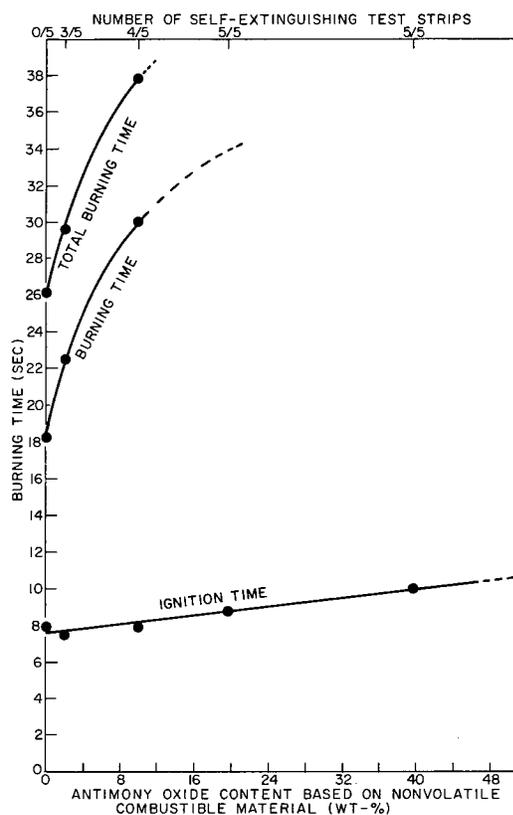


Fig. 3 - Effect of antimony oxide content on fire retardancy, for an acrylic latex paint containing 24.8 wt-% aliphatic chlorine based on nonvolatile combustible solids

Some of our initial studies in fire-retardant additives were with liquid chlorinated biphenyl and polyphenyls, and in particular, a material designated Aroclor 1254. This material is a viscous liquid and contains approximately 54 wt-% aromatic chlorine. Because of its lower chlorine content, the Aroclor was less effective on a gram-for-gram basis than the Unichlor. Thus, to introduce appreciable fire retardancy into the formulation, a larger amount of the Aroclor had to be used. At these high levels, the paint remained tacky and thus was impractical.

Table 5 summarizes the composition of the paints used in evaluating the effectiveness of Aroclor 1254 as a fire retardant. It will be recalled that when Unichlor 70B was used as the chlorine source (Figs. 2 and 3) it was not considered as part of the combustible solids, since it did not burn. On the other hand, Aroclor 1254 will burn when exposed to a flame. However, since the Aroclor will self-extinguish when the flame is removed, it would have to be considered as a very poor fuel. Therefore, for the purpose of this discussion, the Aroclor will not be considered as part of the nonvolatile combustible solids.

From Fig. 4 it can be seen that increasing the chlorine content by adding more Aroclor to a series of formulations containing no antimony oxide gives only a slight improvement in fire retardancy. None of the formulations are self-extinguishing, and the total burning time increases from 22 sec for a formulation containing no chlorine to only 27 sec for one containing 46 wt-% chlorine, based on the weight of nonvolatile combustible solids.

Even in the presence of antimony oxide, the Aroclor does not appear to be an efficient fire-retardant additive. From Fig. 5 it can be seen that adding varying amounts of antimony oxide to a series of formulations containing 23 wt-% chlorine results in little or no increase in the total burning time over the formulation containing no antimony oxide. Although the initial addition of antimony oxide does cause one out of five (1/5) samples to self-extinguish, further increase in the antimony oxide content has no effect.

Although the data are not directly comparable, the aromatic chlorine (from the Aroclor) does not appear to be as effective as the aliphatic chlorine (from the Unichlor) on an equal weight basis. Thus, in one case where the antimony oxide and chlorine contents were approximately the same (24 wt-% chlorine and 11.8 wt-% antimony oxide of the combustible material), the aliphatic chlorine resulted in a total burning time of 36 sec and between 3/5 and 4/5 of the samples were self-extinguishing, while the aromatic chlorine gave values of 25 sec and 1/5, respectively.

Although solid Aroclors of higher chlorine content could be used to eliminate the problem of tackiness caused by using the liquid Aroclor and to increase the weight of chlorine per weight of additive, further study with them was not pursued because of their additional drawback of greater toxicity and the necessity of making the fire-retardant additive a greater percentage of the total formulation.

Based on the fire-retardancy test results just presented, the amounts of chlorine and antimony oxide have been tentatively selected at 34 and 14 wt-%, respectively, based on the weight of nonvolatile, combustible material in the paint. This would correspond to approximately 20 wt-% of Unichlor 70B and 6 wt-% antimony oxide based on total nonvolatile solids. Small changes in these amounts may be necessary for optimizing the overall paint performance.

Because titanium dioxide has approximately five times the hiding power of antimony oxide, a reduction in hiding can be expected when part of the titanium dioxide is replaced by antimony oxide. However, since only 15 vol-% titanium dioxide need be replaced, the decrease in hiding would amount to only slightly more than 10% at most. If more pigment is added to increase hiding, gloss will be reduced.

The addition of the chlorinated paraffin to the formulation has been troublesome. Although the chlorinated paraffin is an organic material and somewhat resinous in nature, it appears to behave in the dried paint film as an extender pigment rather than as part of the continuous phase. That is, the resinous particles do not appear to coalesce with the acrylic resin but seem to remain as an inert dispersed phase in the film. This behavior is reflected in the loss of gloss and increased hardness and brittleness of the dried paint film.

Table 5  
Nonvolatile Solids Composition of Formulations Used in Obtaining Data for Figs. 4 and 5

	Figure 4 Parts by Weight				Figure 5 Parts by Weight				
	I	II	III	IV	III	IV	V	VI	VII
Titanium dioxide (R-100)	70.0	70.0	70.0	70.0	70.0	70.0	68.2	65.6	61.2
Antimony oxide (KR grade) Vehicle*	0	0	0	0	0	0	1.8	4.4	8.8
Aroclor 1254 (54% Cl)	75.5	75.5	75.5	75.5	75.5	75.5	75.5	75.5	75.5
	0	21.0	32.0	64.0	32.0	32.0	32.0	32.0	32.0
Total	145.5	166.5	177.5	209.5	177.5	177.5	177.5	177.5	177.5
Wt-% solids in paint	51	55	56	60	56	56	56.3	56.3	56.3
Pigment volume content	22	18	17	14	17	17	17	17	17
Wt-% Aroclor in total solids†	0	12.6	18.0	30.5	18.0	18.0	18.0	18.0	18.0
Wt-% chlorine in total solids†	0	6.8	9.7	16.5	9.7	9.7	9.7	9.7	9.7
Wt-% antimony oxide in total solids†	0	0	0	0	0	0	1.0	2.5	5.0
Wt-% chlorine of combustible solids†	0	15	22.9	45.8	22.9	22.9	22.9	22.9	22.9
Wt-% antimony oxide of combustible solids†	0	0	0	0	0	0	2.4	5.8	11.7
Wt-% combustible solids† in total solids†	51.9	45.3	42.5	36.0	42.5	42.5	42.5	42.5	42.5

\*The vehicle includes acrylic resin, thickener solids, defoamer, grinding vehicle solids, etc.

†The total solids includes pigments, vehicle\*, and Aroclor.

‡The combustible solids includes only the vehicle\*.

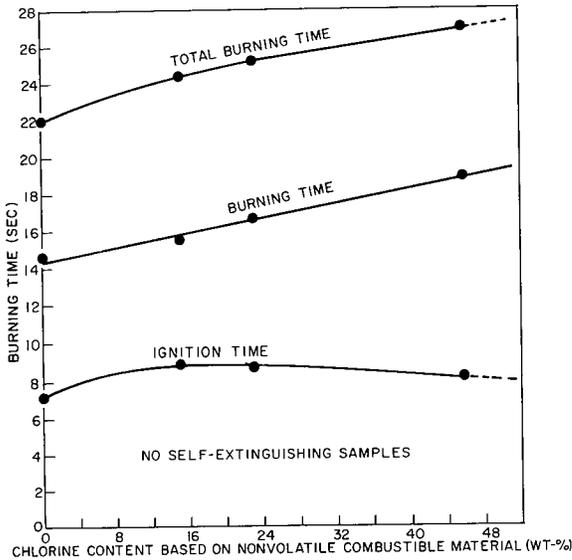
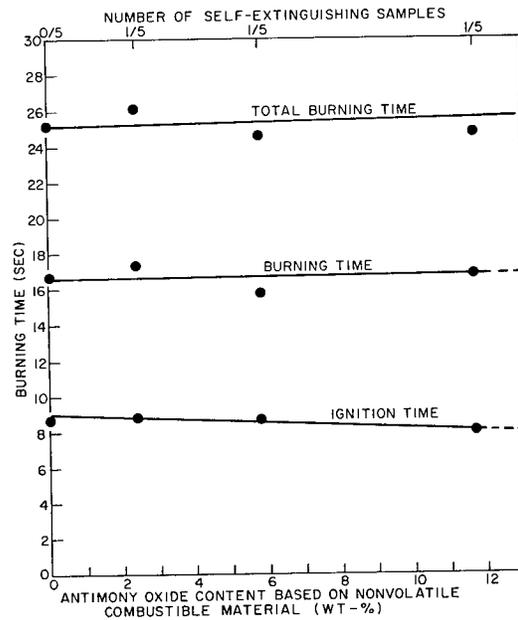


Fig. 4 - Effect of aromatic chlorine content on fire retardancy, for an acrylic latex paint containing no antimony oxide

Fig. 5 - Effect of antimony oxide content on fire retardancy, for an acrylic latex paint containing 22.9 wt-% aromatic chlorine based on nonvolatile combustible solids



Because of this behavior, the titanium dioxide-antimony oxide pigment concentration had to be reduced to approximately 16 vol-% to obtain a gloss of even 29%. The gloss of the NRL acrylic was approximately 65% at a pigment concentration of 21 vol-%. Because of the increased hardness resulting from the addition of the chlorinated hydrocarbon, the ratio of the soft acrylic resin (Rhoplex B60A) to the hard acrylic resin (Rhoplex C72) had to be increased from 1.400 to 3.43 in order to maintain adequate flexibility of the dried paint film on the Ensolute. In addition, if the organic liquid additives (carbitol, polyglycol P1200, and pine oil) come in contact with the chlorinated paraffin before either is well wetted with the water, the chlorinated paraffin will be attacked by these solvents and become tacky. The titanium dioxide pigment particles will therefore stick to the chlorinated paraffin, causing formation of small aggregates or lumps in the paint.

It was also necessary to vary the amount and type of surfactants to obtain bubble- and foam-free coatings. This change, along with the increase in the ratio of the soft acrylic to hard acrylic resins and the addition of the chlorinated paraffin would be expected to affect the abrasion and water resistance of the coating. Attempts to obtain comparative data with the Gardner Model 105 Straight Line Washability and Abrasion Machine have been only partially successful. The main problem has been a failure in adhesion between the top white coats undergoing evaluation and the green chlorinated alkyd used as the undercoat. Thus, in several of the evaluations, the top coat has peeled up before wearing through to the green undercoat. Since the particular batch of chlorinated alkyd used was several years old, the poor adhesion may be attributed to some deterioration in this paint during storage. The NRL acrylic which has previously shown good adhesion to the chlorinated alkyd paint also failed several times in this manner. That this batch of chlorinated alkyd paint had changed with age was further indicated by its low gloss (28%) compared to specification (35 to 50%). Therefore, these evaluations will be repeated with a fresh batch of the chlorinated alkyd. However, qualitatively the NRL acrylic modified with the chlorinated paraffin and containing a larger amount of the soft resin was equal to or better than the presently approved commercial water-base, fire-retardant paints, but inferior to the basic NRL acrylic paint and the chlorinated alkyd (Formula 124/58). Our latest modified formulation is shown in Table 6; however, it should be pointed out that further changes in this formulation are being made to optimize the paint properties and performance.

Table 6  
Experimental Acrylic Latex Fire-Retardant Formulation\*

Ingredients	Function	Wt-%
<u>Premix</u>		
1. Titanium dioxide (R-100)	Pigment	17.9
2. Antimony oxide (KR grade)	Pigment	3.2
3. Tamol 731 (25%)	Surfactant	0.59
4. Eldefoam 2892	Antifoam	0.14
5. G-11 (hexachlorophene)	Preservative	0.08
6. Unichlor 70AX	Fire retardant	10.07
7. Water	Thinner	10.3
<u>Let Down</u>		
8. Rhoplex B60A (45%)	Vehicle	36.2
9. Rhoplex C72 (45%)	Vehicle	11.4
10. Carbitol	Coalescing aid	4.0
11. WSR-301 (4%)	Thickener	4.5
12. Polyvinylpyrrolidone (20%)	Thickener	1.2

\*Constants  
 Total solids: 53.9%  
 Pigment volume content: 16.2%  
 Gloss (60°): 29 %

Vinyl Chloride-Acrylic Copolymer Latex

Because of the numerous problems caused by the addition of the chlorine-containing additives to the NRL acrylic latex, a film-forming polymer in which the chlorine is chemically combined with the polymer is also under investigation. It was hoped that a vehicle based on a vinyl chloride-acrylic copolymer would retain many of the desirable film

characteristics of the acrylic resin as well as provide a source of halogen necessary for fire retardancy. Initial studies have been made with a latex manufactured by the Goodyear Tire and Rubber Company called Pliovic 400. This material contains approximately 30 wt-% chlorine, which would be sufficient, in the presence of antimony oxide, to yield a self-extinguishing paint.

Initial problems in the development of a Pliovic 400 based paint were in severe bubble and foam formation and mud-cracking. Solution of these problems through proper choice of surfactants and thickening agents has resulted in formulations with gloss in the range of 45%. The scrub resistance of these formulations appears to be equal to or better than the approved fire-retardant, water-based paints. However, freeze-thaw stability is poor based on the evaluation of a single formulation which would not pass even one cycle. The toxicity of these formulations would be expected to be of the same order of magnitude (very low) as the latex paints previously discussed.

The fire retardancy of this formulation was excellent. A burning sample would immediately self-extinguish when the flame of the microburner was removed.

A typical formulation is shown in Table 7. Again, it should be realized that this is not a final formulation and that further changes will be made to obtain maximum performance.

Table 7  
Experimental Vinyl Chloride-Acrylic Latex,  
Fire-Retardant Formulation\*

Ingredient	Function	Wt-%
<u>Premix</u>		
1. Titanium dioxide (R-100)	Pigment	21.0
2. Antimony oxide (KR grade)	Pigment	3.9
3. Tamol 731 (25%)	Surfactant	0.60
4. Tetrapotassium pyrophosphate	Dispersant	0.14
5. Triton CF-10	Surfactant	0.09
6. Water	Thinner	8.8
7. Eldefoam	Antifoam	0.27
<u>Let Down</u>		
8. Pliovic 400 (48%)	Vehicle	60.0
9. Butyl carbitol acetate	Coalescing aid	2.8
10. Igepal CO-630	Surfactant	0.10
11. Eldefoam	Antifoam	0.09
12. WSR 301 (4%)	Thickener	1.8
13. Polyvinylpyrrolidone	Thickener	0.49

\*Constants

Total solids:	54.1%
Pigment volume content:	23.7%
Gloss (60°):	38 %

#### FUTURE WORK

Efforts will be made to further improve the properties and performance of the two basic formulations just discussed, the Rhoplex formulation and the Pliovic formulation.

It also is planned to investigate a third system based on a water-soluble resin. However, the success of such a system will depend on the development of a water-soluble, fire-retardant polymer capable of being cured under ambient conditions to a water-insoluble film.

## REFERENCES

1. Miller, R.R., and Piatt, V.R., "The Present Status of Chemical Research in Atmosphere Purification and Control on Nuclear-Powered Submarines," NRL Report 5465, Apr. 1960, (a) pp. 73-79, (b) pp. 1-14
2. BuShips Instruction 9190.40 Change Transmittal 3, "Nuclear Submarines - Reduction of Atmospheric Contamination," July 25, 1963
3. National Paint, Varnish and Lacquer Association, Inc. "Guide to U.S. Government Paint Specifications - MIL-P-17970B"
4. Bureau of Ships Technical Manual NAVSHIPS 250-000, Chapter 9190, Section IV, Part 4, 9190.122, 1d, June 1, 1963
5. BuShips Trip Report SSR(N)586 Ser 649B-2761 of Nov. 5, 1960
6. USS HALIBUT (SSG(N)587) ltr 9190/dkd, Ser 823 of Dec. 15, 1960, to NRL
7. USS THOMAS A. EDISON (SSB(N)610) ltr of May 22, 1964

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13. ABSTRACT Efforts have been made to develop a high-quality interior paint for nuclear-powered submarines. Because of the circumstances under which the paint is to be used, it must have properties not previously required for ships in the fleet. It should (a) release little or no toxic or organic material to the atmosphere as it is applied or as it dries, (b) be self-extinguishing in its fire-retardancy performance, (c) have a gloss in the medium range (50% at a 60° angle), (d) be flexible and (e) have a highly decorative appearance in general. Chlorinated compounds and antimony oxide were used to introduce fire retardancy into an acrylic latex paint; however, they also affected the physical appearance and performance of the paint. The highest degree of fire retardancy and best overall properties were obtained when a chlorinated paraffin and antimony oxide were used together. The tentative concentrations have been selected as 34 wt-% for chlorine and 14 wt-% for antimony oxide, based on the weight of nonvolatile, combustible material in the paint. Further changes are being made in this formulation to improve performance. A film-forming polymer which contains chlorine chemically combined with the polymer was studied, and a formulation was devised making use of this material. It is also undergoing further examination.		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fire retardancy Nuclear-submarine habitability Submarine paints Self-extinguishing paints Nontoxic paints Chlorinated compounds Antimony oxide Water-base paints						

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