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Nature and Chemical Stability of Halowax Compounds

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ABSTRACT

Corrosion and deterioration of some types of naval radio and electrical equipment have been observed under hot, humid climatic conditions. These units have utilized, as one type of dielectric material, chlorinated naphthalene products known commercially under the name of Halowax, as potting, sealing and impregnating compounds.

The cause of this chemical breakdown was suspected to be the hydrolytic decomposition of the Halowax producing hydrogen chloride. The hydrochloric acid thus formed would be extremely active in corroding metal and in promoting further breakdown of the Halowax, as well as destroying its dielectric properties.

A test for hydrolytic breakdown of chlorinated compounds has been previously developed in this laboratory in connection with the study of liquids to be used as non-inflammable hydraulic fluids and is described in NRL Report P-2009. This test and others have been applied to a study of the stability of the Halowaxes.

Several types of Halowax have been investigated from the viewpoint of potential corrosion to radio equipment. Many Halowax preparations were found unsatisfactory because of the production of hydrochloric acid under mild hydrolytic conditions. Some Halowaxes were found to be stable and non-corrosive under the test conditions.

It is recommended that a hydrolytic stability test be used to eliminate from consideration any chlorinated impregnants which are unstable under mild hydrolytic conditions. It is further recommended that an electrical test for breakdown be made to test stability of non-chlorinated compounds and as a further check on chlorinated compounds. The test used by the Bell Telephone Laboratories using impregnated paper between aluminum electrodes is particularly sensitive and accurate. The electrical test may not be necessary for Halowax compounds used as cable impregnants since it is not imperative that all minor corrosion be eliminated with this type of equipment.

INTRODUCTION

(a) Authorization

1. This research was authorized by a Bureau of Ships Project No. 419/43.

(b) Statement of Problem

2. Compounds used and sold under the trade name "Halowax" have been used extensively in naval radio and electrical equipment as potting, sealing and impregnating compounds. Certain units of naval radio and electrical equipment, known to contain one or more Halowaxes as dielectric materials have been observed to be subject to corrosion and deterioration, especially under hot, humid climatic conditions. The electrical failure was thought to be due to the hydrolytic breakdown of a Halowax dielectric, producing corrosive substances; hence the chemical study of the stability of these products was undertaken. This report covers investigations made to determine which Halowax products will withstand these extreme climatic conditions and to determine to what extent decomposition of these Halowaxes may be expected to occur.

3. During the course of an investigation of proposed synthetic hydraulic oils, it was found necessary in this laboratory to devise a test for hydrolytic stability of chlorinated compounds. This test was found to be directly applicable to the problem of hydrolytic breakdown of Halowaxes since the same fundamental chemical reactions were involved.

(c) Known Facts Bearing on the Problem

4. According to information supplied by the Halowax Division of the Union Carbide and Carbon Corporation, the term Halowax refers to many products of different constitution produced commercially by their company. There are many basic Halowax products used as components of the commercial mixtures also sold under the trade name of Halowax. These basic products differ in degree of chlorination and consequently in physical properties. Four principle ones are Halowaxes #1000, #1012, #1013 and #1014. Halowax #1000 is a liquid containing 25-28% chlorine and corresponds approximately to a mixture of mono-(21.9% Cl) and di-(36% Cl) chloronaphthalene. Halowax #1012 is a crystalline solid containing 46-49% chlorine and corresponds roughly to a tri-(46% Cl) chloronaphthalene. Halowax #1013 is a solid containing approximately 56% chlorine, which corresponds to a mixture of tetra-(53.4% Cl)

and penta-(59.0% Cl) chloronaphthalene. Halowax #1014 is an amorphous solid containing 62-64% chlorine which corresponds to hexa-(63.6% Cl) chloronaphthalene. These four products are relatively pure since they are distilled materials. The crude Halowaxes from which these better preparations are made are sometimes used themselves as basic components, especially as ingredients of cable impregnants.

5. Some of these less pure Halowaxes are as follows: Halowax #1005 is the crude black chlorination product from which Halowax #1013 is distilled. Halowax #1006 is the crude product from which Halowax #1014 is distilled and Halowax #1011 is the crude oil from which Halowax #1000 is distilled.

6. The basic Halowax products are not used extensively as such, but are usually compounded with other materials to make the various commercial preparations. The compounded products still retain the name Halowax, but are designated by different numbers. The numbering system used is not as informative as many other commercial product nomenclatures such as that used by the Monsanto Chemical Co. to designate aroclors, but it does serve to distinguish between the several classes of Halowax preparations.

7. Four series of numbers are used, the 1000 series, the 2000 series, the 3000 series, and the 4000 series. The 1000 series comprises the basic Halowax products already mentioned, mixtures of two or more of the basic products and the crude chlorination products from which the basic products are distilled.

8. The 2000 series consists of a large number of compounded products made from either the basic Halowax products or the crude materials of the 1000 series together with a wide variety of waxes, resins, asphalts, dyes and solvents. Each member of the 2000 series is usually custom-made to fit the requirements of one particular cable manufacturer or other user of the product. The materials that are added to make the members of the 2000 series from the 1000 products are selected for several reasons. Materials are added for such purposes as to destroy the crystalline character, to change the melting point, to modify the hardness, to change the electrical properties, to make it easier to apply, or to give the product a characteristic color.

9. A few of the Halowax products of the 2000 series that are used on radio equipment are:

Halowax #2012 - Made from #1013 + petroleum wax (Cerese AA)

Halowax #2141 - Made from #1014 + polyisobutylene

Halowax #2002 - Made from #1013 † Gilsonite Serox (Mexican Asphalt)

Halowax #2004 - Made from #1014 † Gilsonite Serox (Mexican asphalt of a higher m.p. than #2002).

10. Another of the Halowax products that has recently come to the attention of this Laboratory in connection with a problem of cable saturants was learned to be another of the 2000 series of Halowax products, #2034. This material was encountered in an investigation of the effect of Halowax on the polyvinyl chloride wire coating, both of which were used in cable manufacture. Halowax #2034 is a mixture of #1014 with several chlorinated diphenyls and polystyrene. The mixture is applied in toluene solution with the solvent being later evaporated in the drying operation at 80°C.

11. Many of the Halowax products used as cable saturants are included in the 2000 series, but detailed information regarding the composition of each one was not obtained. However, if the composition of any specific one is needed, it can be obtained through the Halowax Division of the Union Carbide and Carbon Corporation although it is not the policy of the company to give actual percentage composition unless specifically requested.

12. The 3000 series of Halowax products are the so-called non-toxic Halowaxes. They contain little or no chlorine. It is known and admitted by the Halowax representatives that the chlorinated aromatics, particularly those of high chlorine content, above 50%, are toxic causing liver degeneration and also dermatitis. Cases of dermatitis are most prevalent among workers in cable factories and among shipyard workers where the cable is being installed in confined spaces. The non-toxic Halowaxes usually consist of pitches or asphalts plasticized with some material such as tri-cresyl phosphate. The non-toxic materials are usually cheaper than those containing the chlorinated aromatics, but do not have the flame-proof and desirable electrical qualities of the latter.

13. The 4000 series comprises the chlorinated paraffin products. These products may consist only of chlorinated paraffin as in the case of Halowax #4001 (42-46% Cl), or they may be compounded with resins and fillers to give the desired physical properties. The 4000 series of Halowax are used chiefly for flame-proofing and water-proofing fabrics. An important naval application of these #4000 compounds is in the flame proofing of life-preservers.

14. Only pure dyestuff naphthalene is used for the manufacture of the chlorinated naphthalene. The purity of the raw material is checked by melting point, but the most accurate check on the purity is by actual chlorination. Samples of naphthalene representing a carload are received at the Halowax research laboratories at Bloomfield, N. J. from the Barrett Company and are chlorinated. The chlorinated material is neutralized and distilled and the products of distillation examined. It is claimed that this procedure is very effective in disclosing any aliphatic part of the original raw material since the halogen on the aliphatic part of the original raw material is much less stable than on the aromatic. If the sample proves to be acceptable, the car is shipped to the manufacturing plant at Wyandotte, Michigan and another sample chlorination run there before the car is emptied.

15. In the actual manufacture, the naphthalene is subjected to varying degrees of chlorination depending on the type of product desired. When the reaction has reached the desired stage, the process is stopped and the acid that has been liberated during chlorination is neutralized with lime. The insoluble material is removed by filter pressing, yielding a black substance containing less than 1% insoluble material. This is the crude material described earlier as one of 1005, 1006, or 1011 from which the pure basic Halowax product is distilled. Care is taken during the chlorination to prevent addition of the halogen and to permit only the substitution reaction to proceed.

16. Chlorinated diphenyls are used with the chlorinated naphthalene in many of the Halowax products. The Halowax Products Division of Union Carbide manufactures the chlorinated diphenyls used in their products and designates them by numbers, the last two digits of which indicate the percentage of chlorine. For example, Halowax #1048 is a chlorinated diphenyl containing 48% chlorine. Using the same system, Halowax #1060 would be a chlorinated diphenyl containing 60% chlorine.

17. The Navy uses a larger quantity of Halowax products in electrical cables than for any other purpose. For this use, the flame-proof quality, the high electrical resistance and the water-proof quality are the chief advantages. The toxicity is one of the main disadvantages. Halowax, as used in cable, is not usually applied directly to the wire, but as an impregnant of asbestos used over the primary insulation or wire coating. In this case, it is applied as a toluene solution and dried at low temperatures. Some of the so-called non-toxic Halowax products are also used in cable manufacture.

18. In electrical and radio equipment, Halowax products are used in condensers, transformers, reactors, coils, etc. Although the pure chlorinated naphthalene is still used to a limited extent as a condenser dielectric, the chief use in electrical equipment is as a potting and sealing compound. The wiring is usually covered with an insulating varnish and the Halowax product used over that. There is at least one manufacturer, however, who impregnates coils directly with a Halowax of the 2000 series. For electrical equipment, no solvent is used with the Halowax. The parts to be treated are dipped in the Halowax at 120° to 150°C after thorough vacuum drying. The Halowax manufacturer stresses the necessity of having the equipment thoroughly dry before dipping, potting or sealing.

19. Halowax products of the 4000 series, chlorinated paraffins and mixtures with other substances, are used as flame-proofing and water-proofing agents for fabrics. The chlorinated paraffins are much less stable than the chlorinated aromatics so that these products are likely to liberate hydrochloric acid readily under humid conditions. In the Army specifications for the fabric-treating material, calcium carbonate is included to help neutralize the decomposition products of the Halowax 4000 mixtures.

20. Chlorinated naphthalenes (Halowaxes) are used in cutting and breaking-in oils and in extreme pressure, (E. P.), lubricants. Chlorinated paraffin Halowaxes are used in hypoid gear lubes and to increase the film strength of lubricants.

21. Halowax numbers which are hyphenated such as 1-67 refer to experimental samples whose composition is known only to the Halowax manufacturers. These samples are given a number which conforms to the remainder of the series when an acceptable composition is found for the user of the dielectric material. The last three digits in a number such as 2014 refer to a specific product manufactured to meet some company's specifications, and are entirely empirical and contain no key to the composition of the wax. This should be ascertained by direct inquiry to the Halowax Products Division.

22. The manufacturers of Halowax products specify that each Halowax should be applied to wire only over a good lacquer and with strict exclusion of moisture. Some manufacturers of electrical equipment fail to comply with this recommendation, according to the Halowax Division.

23. An extensive investigation of the use of halogenated hydrocarbons as dielectric paper impregnants was made by the Bell

Telephone Laboratories.¹ They have studied the behavior of Halowax #1001 (chloronaphthalene) and Arochlor #1254 (chlorinated diphenyl containing 54% chlorine) when used as impregnants for paper in electrical apparatus such as capacitors and transformers. Samples of Kraft paper and rag stock linen paper were dried and impregnated with hot dielectric compound. The impregnated papers were fastened between metal foils and a d.c. potential was applied. The conductance was then observed for an extended period until breakdown occurred. It was found that breakdown at 400 volts d.c. potential was observed often after 20 to 60 hours when the temperature was 100°C using aluminum foil electrodes. Similar breakdown was observed at lower temperatures, but here it proceeded at a decreased rate. It was found that Kraft paper showed better stability than linen paper in these tests. These authors explain their results by attributing the breakdown to a splitting off of hydrochloric acid from the impregnant or as a direct result of the degrading influence of the electrode metal upon the chlorinated compound. The hydrochloric acid formed then attacks the aluminum electrodes by a combination of direct chemical action and electrolysis, forming aluminum chloride which actively catalyzes further decomposition reactions. They point out that hydrochloric acid itself is known to accelerate the decomposition of cellulose materials and in addition adds to the conductivity which finally builds up to a point where thermal effects enter.

24. These results were discussed with representatives of the Halowax Corporation who were well acquainted with them. Conclusions drawn by these representatives were that the Bell Telephone experiments produced failures due to hydrolytic instability which was present because the specimens impregnated were not properly dried before the impregnation treatment. These conclusions were based upon experiments carried out at the Halowax research laboratories at Bloomfield, N. J. and have not been published.

25. The Bell Telephone report states that the materials used in their experiments were dried until the moisture content of the paper was less than 0.05% by weight and the application was done by a process of vacuum impregnation at 110-120°C. Truth as regards the obvious differences of opinion between the two concerns involved could not be ascertained.

(d) Theoretical Considerations

26. Halowaxes used in naval equipment contain large percentages of chlorine. Hydrolytic and thermal breakdown of the Halowax containing compounds of the chlorinated aromatic type can produce the highly corrosive substances, chlorine and hydrochloric acid.

The traces of hydrochloric acid formed would readily attack the metal and by the resulting high conductivity of the dielectric, would destroy the insulating effect of the Halowax in which it would be formed. A further reaction to be expected from the liberated acid would accelerate chemically the further decomposition of the Halowax. In addition to the chloride produced, other ionic material may be developed which reduces the electrical resistivity of the Halowax and would be exceedingly corrosive especially in the presence of an electrical potential. A measurement of the chloride and other ionic material developed during hydrolysis would be expected to be a positive indication of the tendency of a given Halowax to corrode metal and subsequently produce equipment breakdown.

(c) Narrative of Original Work Done

27. A trip to confer with Mr. Intemann and Mr. Maybower of the Halowax Products Division, Union Carbide and Carbon Corporation was made by Lt. J. M. Fogelberg and Dr. John K. Wolfe on March 12, 1943. Information was obtained relative to the nature of the Halowax products, the raw materials used and the method of manufacture of the basic products, the composition and properties of the basic products and of the compounded materials. The naval uses of Halowax products were enumerated as well as the chemical nature of material furnished in each case. The nomenclature system used for the commercial preparations was ascertained. The methods of application as well as questions of stability and corrosion of metals by Halowax products were discussed. A visit was also made to the Materials Laboratory, Brooklyn Navy Yard and the work being done there on the testing of material containing Halowax was discussed with Lt. Comdr. Barsky, Ass't Laboratory Officer and Messrs. Fraser and Graves of the Electrical Division.

28. A number of Halowaxes of the 1000 and 2000 series were secured, with particular emphasis on obtaining material used commercially as coil, capacitor and cable impregnants. These were tested as received for the presence of free chloride ion by extracting a toluene solution of the wax with dilute sodium bicarbonate and analyzing the aqueous bicarbonate solution for chloride by the Volhard method.² A similar analysis was made after refluxing for four hours the toluene solution of Halowax with a dilute bicarbonate solution. This second, or hydrolytic breakdown test, was repeated in the presence of steel, copper, brass and dural 17ST, so that the effect on the metal could be observed and the catalytic effect of the metal on the Halowax breakdown could be ascertained.

29. The total ionic material developed in the hydrolysis was determined by replacing the bicarbonate solution with distilled water and measuring the conductivity of the water after refluxing.

30. The thermal stability was tested in experiments which involved maintaining the Halowax at an elevated temperature (137-138°C) for 72 hours and then studying the breakdown resulting by application of the hydrolysis test.

METHODS

(a) Apparatus

31. The hydrolytic breakdown test used was a modification of that described in NRL Report No. P-2009⁴ for the testing of liquids under consideration as base fluids for use as synthetic non-inflammable hydraulic oils. The test was made using a 250 ml. round bottom flask fitted to a reflux condenser by means of a ground glass joint. Heating was accomplished by a Bunsen burner placed at the base. Boiling chips were used to promote smooth refluxing of the water, toluene, Halowax mixture.

32. In the hydrolytic breakdown test for total ionic material certain additional precautions were observed. Boiling chips were omitted and steam was employed as a source of heat to avoid bumping of the mixture. All apparatus was carefully washed with distilled water before using. The use of ground glass joints rather than cork or rubber stoppers was essential since the exclusion of ionic substances was imperative.

33. The heat treatment apparatus is shown in Plate 10. "A" is an 18 mm. tube which contained the sample to be heated. The sample is introduced through opening E. Tube A is surrounded by a round bottom flask which is attached by ground glass joint B. A reflux condenser is attached at joint C. A liquid having the boiling temperature at which the Halowax is to be heated is introduced into the round bottom flask until the level is just below but not touching the bottom of tube A. On heating the flask, the liquid boils, leaves by side arm D and is refluxed in the condenser. The entire tube A is surrounded by refluxing vapor and the temperature thus remains constant as long as both liquid and vapor are present in the boiling mixture.

(b) Materials

34. The following test solutions and standard solutions were prepared and used in the tests:

(a) Sodium bicarbonate -- A 1% solution of NaHCO_3 c.p. anhydrous in distilled water was used.

(b) Potassium thiocyanate, 0.1 Normal. Ten grams of

KONS, c.p. Crystals Reagent Quality, was weighed roughly and made up to 1 liter in a volumetric flask with distilled water. Standardization was made by titrating suitable aliquots against 0.1 Normal silver nitrate.

(c) Silver nitrate, 0.1 Normal. A carefully weighed sample (16.9890 g.) of c.p. Primary Standard Silver Nitrate was dissolved and made up to 1 liter in a volumetric flask with distilled water.

(d) Ferric Ammonium Alum Indicator Solution. A saturated solution of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ in distilled water was treated with nitric acid until the brown color was discharged. The mixture was then filtered and bottled as indicator.

(c) Experimental Procedure

(A) Hydrolytic procedure

35. The hydrolysis was a modification of that described in NRL Report No. P-2009.4. A 25 cc. sample, when the Halowax was obtained as a toluene solution, or 5 grams Halowax and 25 cc. toluene when the sample was obtained as a solid, was placed in a 250 ml. round bottom flask fitted with a reflux condenser. To this was added 25 cc. of 1% sodium bicarbonate. The mixture was refluxed for four hours, the water solution separated, quantitatively and titrated by the Volhard method for chloride.

(B) Hydrolysis in the Presence of Metal

36. This hydrolysis test was identical with that previously described except that a strip of metal was placed in the round bottom flask. Four types of metal were used, cold rolled steel, copper, brass and dural 17ST. Each strip was carefully prepared by polishing with emery cloth and steel wool and was thoroughly degreased by cleaning in boiling benzene and finally washing with petroleum ether. The strip rested vertically in the flask, with the lower half immersed in the hydrolysis mixture and the upper half exposed to a refluxing vapors. Photographs were made of the strips after the hydrolysis was completed.

(C) Chloride Analysis

37. The titration was carried out by the Caldwell and Moyer modification³ of the Volhard method. The aqueous portion of the hydrolysis mixture was placed in a glass stoppered Erlenmeyer flask. An excess of 0.1 N silver nitrate (20 cc.) was run in

and 6 N nitric acid added dropwise until the silver carbonate dissolved and the mixture was slightly acid. A few cc. of nitrobenzene and twelve drops of ferric ammonium alum indicator were added. The 0.1 N potassium thiocyanate was run in until near the end point. The mixture was then stoppered and shaken vigorously. Titration was continued until the definite pink color of the end point had been observed. The end point was checked several times by alternately adding aliquots, silver nitrate and potassium thiocyanate.

1 ml. of 0.1 N $\text{AgNO}_3 \cong 3.5 \text{ mg. Cl}^-$

38. A blank determination was made for chloride present in all reagents used. The indicator blank for the volume of solution used was determined and subtracted from the total thiocyanate reading. The results of the analysis are expressed as milligrams of chloride ion found in the aqueous layer. Calculation was then made to find the milligrams of chloride ion per milliliter of Halowax solution or per gram of Halowax depending on whether the sample used was a solution or solid.

(D) Conductivity Measurement

39. A 5 gram sample of the Halowax was placed in a 250 ml. round bottom flask with 25 ml. toluene and 50 ml. distilled water. The flask was fitted with a reflux condenser by means of a ground glass joint and heated on a steam bath for four hours. No boiling chips were used. The aqueous layer was removed using a clean separatory funnel and the conductivity measured at 10,000 cycles per second using a General Radio type 716 A bridge and bright platinum electrodes. The result is expressed as ohms resistance of the cell and calculated to the equivalent molality for an aqueous solution of potassium chloride.

(E) Thermal Stability

40. Stability toward heat was measured by keeping the Halowax at 137-138°C for 72 hours using the apparatus shown in Plate 1 and then applying the hydrolytic breakdown test. The liquid used for refluxing in the heat treatment was xylene, selected because of its boiling point. Behavior toward thermal treatment at 183-184°C was also studied using aniline as the reflux liquid.

DISCUSSION OF RESULTS

(a) Hydrolytic Stability

41. Marked variation was shown in the stability of various

Halowaxes toward hydrolysis. The results are shown in Tables 1, 2, and 3. Table 1 lists the results of the tests for free chloride and the hydrolysis tests. Table 2 shows the results of hydrolysis in the presence of metal. As may be seen from Table 1, all of the Halowaxes tested were unsatisfactory except numbers 1012, 1013, 1014, 2068, 2012, and possibly 1000, 2084, 1-67 and 2101. Appreciable values for chloride ion should rule out any Halowax for use on precise electrical equipment since even small amounts of hydrochloric acid may have a corrosive effect on the unit involved.

42. Some of the most promising Halowaxes, judged by the hydrolysis test, along with one poor one for comparison, were given the hydrolysis test in the presence of steel, copper, brass and dural. The chloride values obtained are given in Table 2. The Halowaxes showed some variation with different metals, but the chief interest of this test lies in the degree of corrosion of the metal, which may be seen in Plates 1-9. A key to the plates showing corrosion tests is given in Table 5. Plate 1 is a control run made with sodium bicarbonate, but no Halowax, to show the corrosion to be expected from the action of the bicarbonate solution alone. Plate 1 contains two samples of each kind of metal. The metal strip to the right in each case is a freshly polished specimen and the strip on the left is a similar piece of metal after four hours of refluxing with bicarbonate solution. Plates 2 and 3 show the various Halowax tests with copper. Plates 4 and 5 contain the results using brass, 6 and 7 are of steel, and 8 and 9 the results using dural. In plates 2 to 9 inclusive, the strip at the far left is an example of the freshly polished metal.

43. In most cases the corrosion of the metal in the presence of Halowax was greater than in the presence of bicarbonate solution alone. The Halowaxes in the 2000 series were less corrosive than those in the 1000 series and Halowax 1-67. Halowax 1-67 was consistently corrosive although no chloride was detected. Halowaxes 2068 and 2101 were consistently the least corrosive and also gave off little chloride. The Halowaxes giving off largest amounts of chloride were uniformly very corrosive. Plate 4 does not show the proper contrast with the blank run with bicarbonate, due to the circumstance that the copper was quite uniformly darkened to a purplish brown.

(b) Conductivity Measurement

44. Table 3 shows the results of the conductivity test. Three tests were made. The results are expressed as ohms of resistance of the aqueous layer and the approximate values calculated for the molality of KCl required to give this resistance. The first test gave low values in ohms due to ionic material in the filter paper used. In the last two tests no filter paper was used. There was very good correlation between conductivity

measurements and chloride values. Halowaxes having high conductivity or low resistivity yielded appreciable amounts of chloride and the Halowaxes showing no hydrolyzable chloride gave water layers of high resistance.

(c) Thermal Stability

45. The result of this test is included in Table 1. Halowax 1014 which gave no hydrolyzable chloride by the hydrolysis test, was maintained at 137-138°C for 72 hours and the hydrolysis test then repeated. No hydrolyzable chloride was obtained. A second thermal treatment for 72 hours at 133-134°C yielded a light brown solid which gave a low, but positive value when tested for hydrolytic chloride. This indicates that Halowax #1014 will break down under severe heat, but that under any normal conditions of use even in hot climates it should be thermally stable for an extended period.

CONCLUSIONS AND RECOMMENDATIONS

46. A number of types of Halowax have been investigated from the viewpoint of potential corrosion of radio equipment. Most Halowaxes were found unsatisfactory for use as a coil, capacitor or condenser impregnant where the possibility of contact with water vapor or moist air exists, because of the release of hydrochloric acid under mild hydrolytic conditions. Some Halowaxes were found to be stable and non-corrosive under the test conditions. It is recommended that any Halowax proposed as an impregnant or dielectric for radio equipment be subjected to a hydrolytic stability test. The development of appreciable amounts of chloride should exclude any sample from further consideration. Compounds showing very slight or no traces of chloride in this test may be considered satisfactory as far as corrosion is concerned, provided that proper methods of application are strictly adhered to. These are reported to include a base coating of protective lacquer, thorough drying during application, effective sealing of the apparatus against moisture and maintenance of dipping baths at a temperature only slightly above the melting point of the Halowax. It should be kept in mind that the lack of hydrolytic chloride is not a guarantee that a dielectric such as a Halowax will be satisfactory in service. Many of these materials, some actually sold under the trade name of Halowax, contain little or no chlorine, but still may contain components in the mixture which are unstable.

47. It cannot be stated on the basis of chemical examination alone, whether a given Halowax sample will or will not be troublesome in any particular type of equipment, especially electrical apparatus operating under high electrical potential, under conditions

other than those used in the actual test conducted. Several reasons for this are: (1) The Halowaxes vary widely in the chemical nature of the basic components; (2) There are usually present in Halowax preparations fillers which are normally inert, but under certain conditions can markedly influence the chemical breakdown; (3) The presence of the electrical potential in some types of apparatus may accelerate or decelerate the chemical reaction involved in corrosion and deterioration. It is therefore recommended that compounds which are stable to hydrolytic tests be further studied under prolonged simulated actual use conditions before a decision on the chemical stability of the particular Halowax product in question is made.

48. Not all manufacturers of radio and electrical equipment follow the recommended methods of using the Halowax products. Some of the makers of cheaper equipment are known to dispense with vacuum drying entirely and depend on the temperature of the dipping bath to drive off any absorbed moisture. The specifications for radio equipment might not disclose the use of such a practice, yet it might be the chief cause for the ultimate failure of the equipment.

49. It is further recommended that a laboratory electrical test for breakdown be made in addition to the measurement of the hydrolytic stability on Halowaxes to be used as coil, capacitor, or condenser impregnants. The test used by the Bell Telephone Laboratory with metal foil electrodes on each side of a paper impregnated with the chlorinated hydrocarbon in question should be quite satisfactory. This is thought necessary since the detection of breakdown products can be done much more sensitively by electrical means than by chemical. It is also necessary as a check on the potential corrosibility of a non-chlorine containing Halowax. Some of the Halowax preparations for use in impregnating cables have been reported to give satisfactory operation in service over long periods. These Halowaxes have been found in this laboratory to give small amounts of hydrolyzable chloride in the method herein described.

50. It is, therefore, not considered necessary to obtain these extremely sensitive electrical breakdown tests on Halowax materials to be used as cable impregnants since it is not imperative that all minor corrosion be eliminated with this type of equipment.

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TABLE 1

Hydrolyzable Chloride in Halowax Samples Obtained in Glass Apparatus

<u>Halowax Sample</u>	<u>Percent Solids</u>	<u>Free Cl⁻ in mgm/cc Halowax Sample</u>	<u>Four hours reflux, Hydrolyzable Cl⁻ mgm/cc Halowax Sample</u>
2013	63-68	.275	.376
2069	69-71	.139	.602
2073	49-57	.753	1.167
2101	34-36	.050	.062
1-67	55	<.005	.024
2014	60	<.005	.637
2044	40	.021	1.30
2064	60	.012	0.77
2068	40	<.005	<.005 (16 hrs.)
2141	(100%) (solid)	---	.06 mgm Cl ⁻ /gm
2002	(100%) (solid)	---	.037 mgm Cl ⁻ /gm
2084	"	---	.027 mgm Cl ⁻ /gm
2012	"	---	<.005 mgm Cl ⁻ /gm
1005	100%	---	.49 mgm Cl ⁻ /gm
1006	"	---	.56 "
1012	"	---	<.005 "
1013	"	---	<.005 "
1014	"	---	<.005 "
1000	0% (liquid)	---	.025 mgm Cl ⁻ /cc
1014	(Heated 72 hours at 137-138°C, sealed tube)	<.005	
1014	(Heated 72 hours at 153-154°C, sealed tube)		.080 mgm Cl ⁻ /gm

TABLE 2

Hydrolyzable Chloride in Halowax Samples Obtained in the Presence of Metals

<u>Halowax Sample</u>	Hydrolyzable Chloride (mgm Cl ⁻ per cc, Halowax Sample)			
	Four hours reflux in the presence of:			
	<u>Steel</u>	<u>Copper</u>	<u>Brass</u>	<u>Dural</u>
2068	.012	<.005	<.005	.019
2101	<.005	.101	<.005	<.005
2013	.351	.499	.433	.445
1-67	<.005	<.005	<.005	<.005
1005	.62 mgm Cl/gm	.44 mgm Cl/gm	.60 mgm Cl/gm	.55 mgm Cl/gm
1006	.66 "	.22 "	.82 "	.61 "
1012	<.005 "	<.005 "	<.005 "	<.005 "
1013	<.005 "	<.005 "	<.005 "	<.005 "
1014	<.005 "	<.005 "	<.005 "	<.005 "

TABLE 3

Results of Conductivity Tests

<u>Halowax</u>	<u>First Test</u>		<u>Second Test</u>
	<u>ohms</u>	<u>mg Cl⁻/g</u>	<u>ohms</u>
1005	523	.36	534 = approx. 1.6×10^{-3} molar KCl
1006	440	.32	513
1012	8,180	none	20,560 = approx 3.2×10^{-6} molar KCl
1013	8,120	"	21,140
1014	8,090	"	21,230; 23,180
Distilled water	88,000	"	
Filtered distilled water	----	"	

TABLE 4

Description of the Appearance and Uses of the Halowax Samples

<u>Halowax</u>	<u>Appearance</u>	<u>Use</u>
1000	clear liquid	coil, capacitor and condenser impregnant, and basic component of other mixtures.
1005	black solid	basic component of cable impregnating mixtures. A crude, undistilled product. When distilled it yields Halowax 1013.
1006	black solid	basic component of cable impregnating mixtures. A crude undistilled product. When distilled it yields Halowax 1014.
1012	white crystalline solid	basic component of coil capacitor and condenser impregnants. A distilled product.
1013	white crystalline solid	basic component of coil, capacitor and condenser impregnants. A distilled product.
1014	light yellow solid	basic component of coil, capacitors and condenser impregnants. A distilled product.
2002	black solid	mixture used for coil, capacitor, and condenser impregnant.
2012	tan solid	"
2084	tan toluene solution	"
2141	white waxy solid	"
2014	black solid	cable impregnant
2044	black solid	"
2064	black solid	"
2068	white solid	"
2069	black tar	"
2073	viscous black oil	"
2101	thin red toluene solution	"
1-67	thin black toluene solution	"

TABLE 5

Key to Plates

All refluxed four hours at 100°C with 1% NaHCO₃

Plate 1: S - steel; C - copper; B - brass; D - dural 17ST
No Halowax

Plates 2 and 3 - copper; Plates 4 and 5 - brass; Plates 6 and
7 - cold rolled steel

Plates 8 and 9 - Dural 17ST

The Halowax used with each metal strip is indicated
by the letter shown beneath the strip as follows:

Plates 2,4,6,8

A Control, no Halowax

B Halowax 2068

C Halowax 2101

D Halowax 2013

E Halowax 1-67

Plates 3,5,7,9

A Control, no Halowax

B Halowax 1005

C Halowax 1006

D Halowax 1012

E Halowax 1013

F Halowax 1014



D



B



C



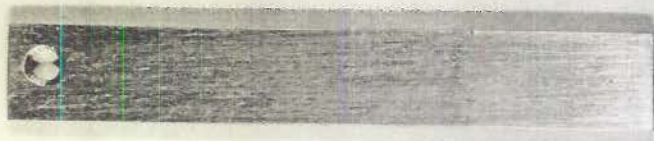
S



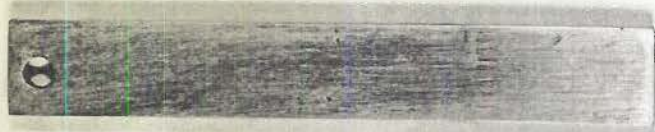
E



D



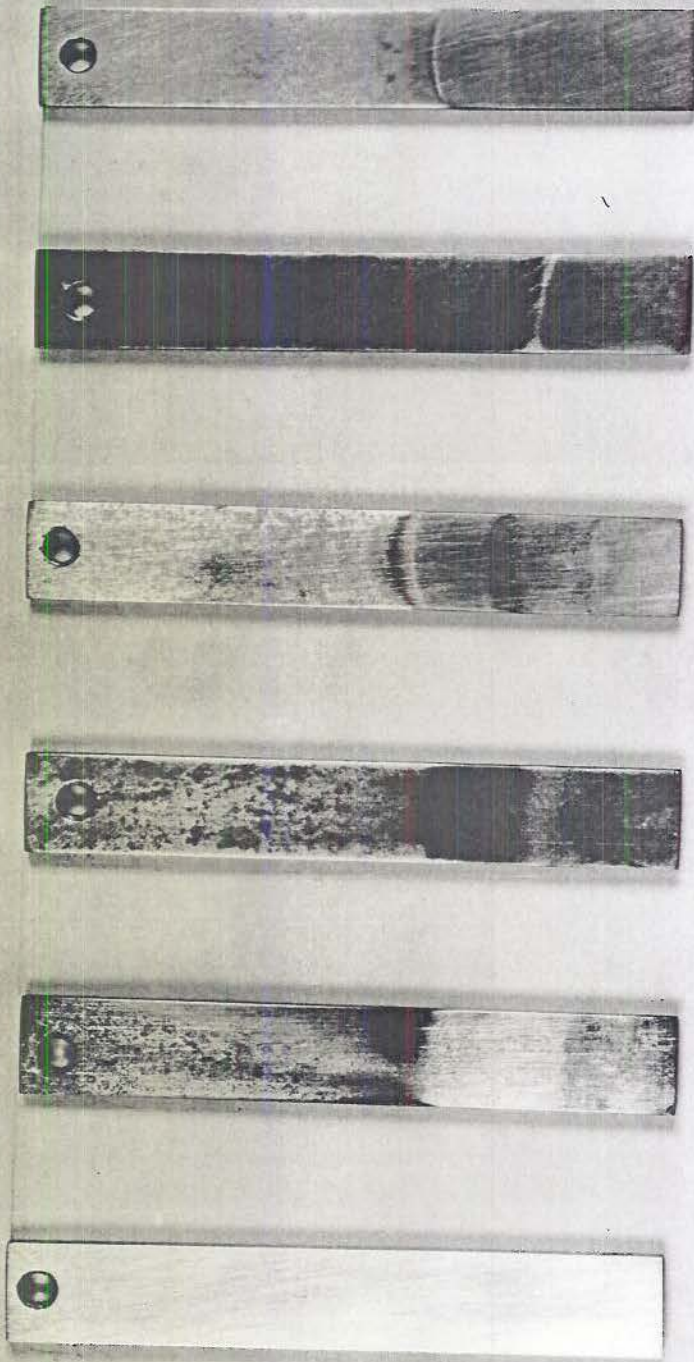
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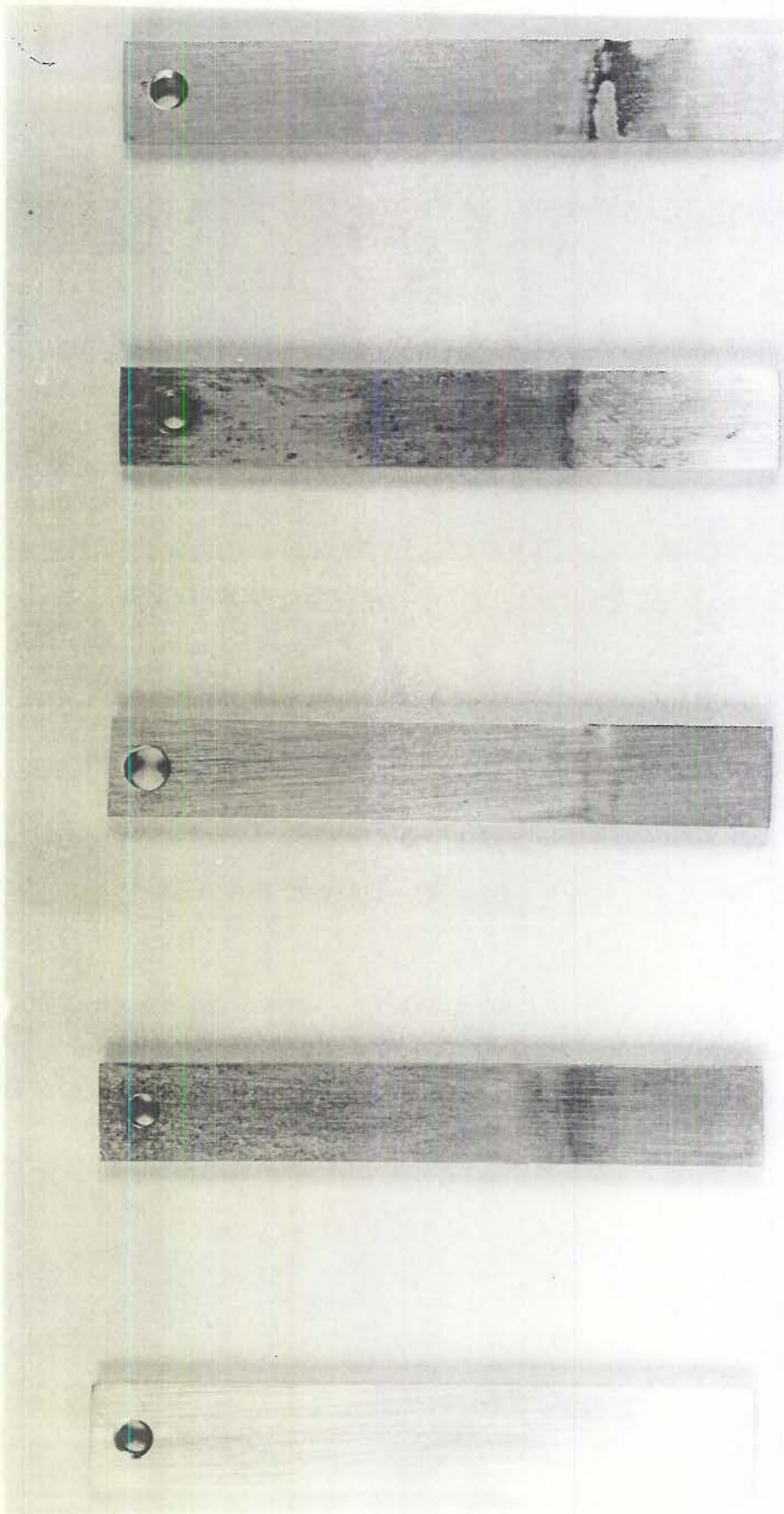
B



A



A B C D E F



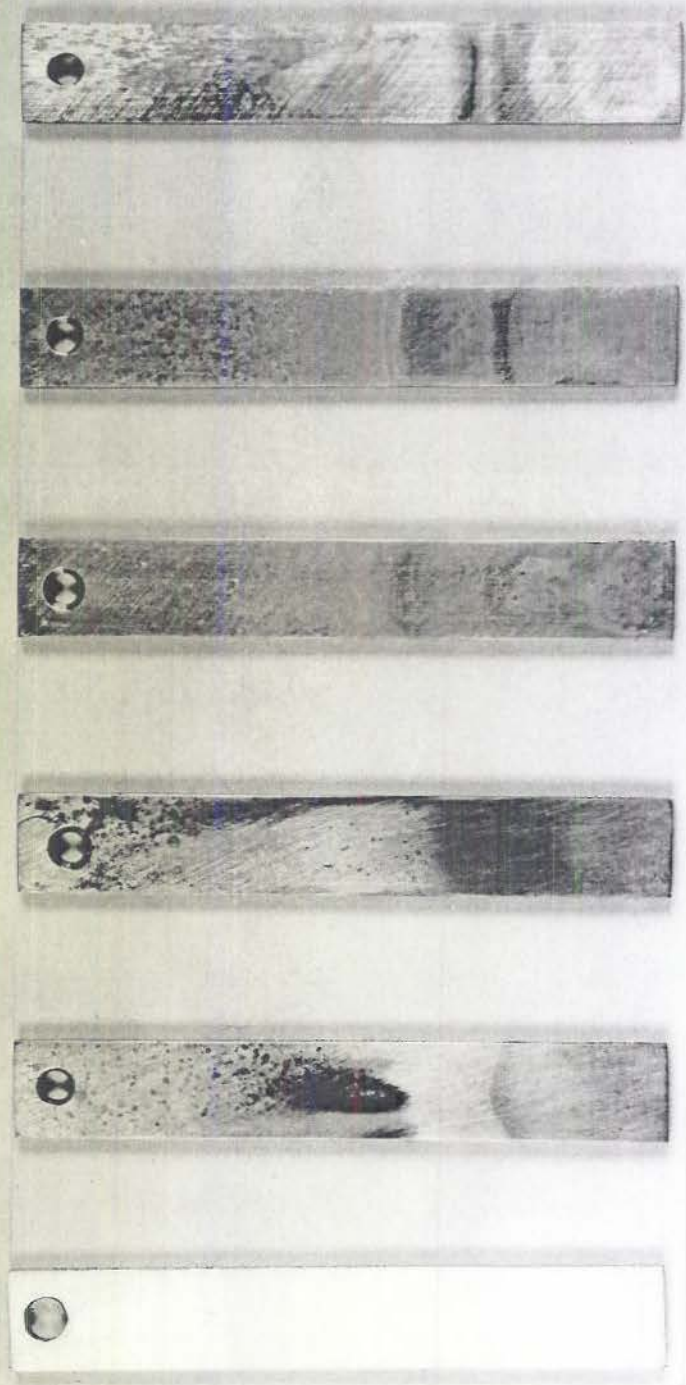
E

D

C

B

A



F

E

D

C

B

A



A



B



C



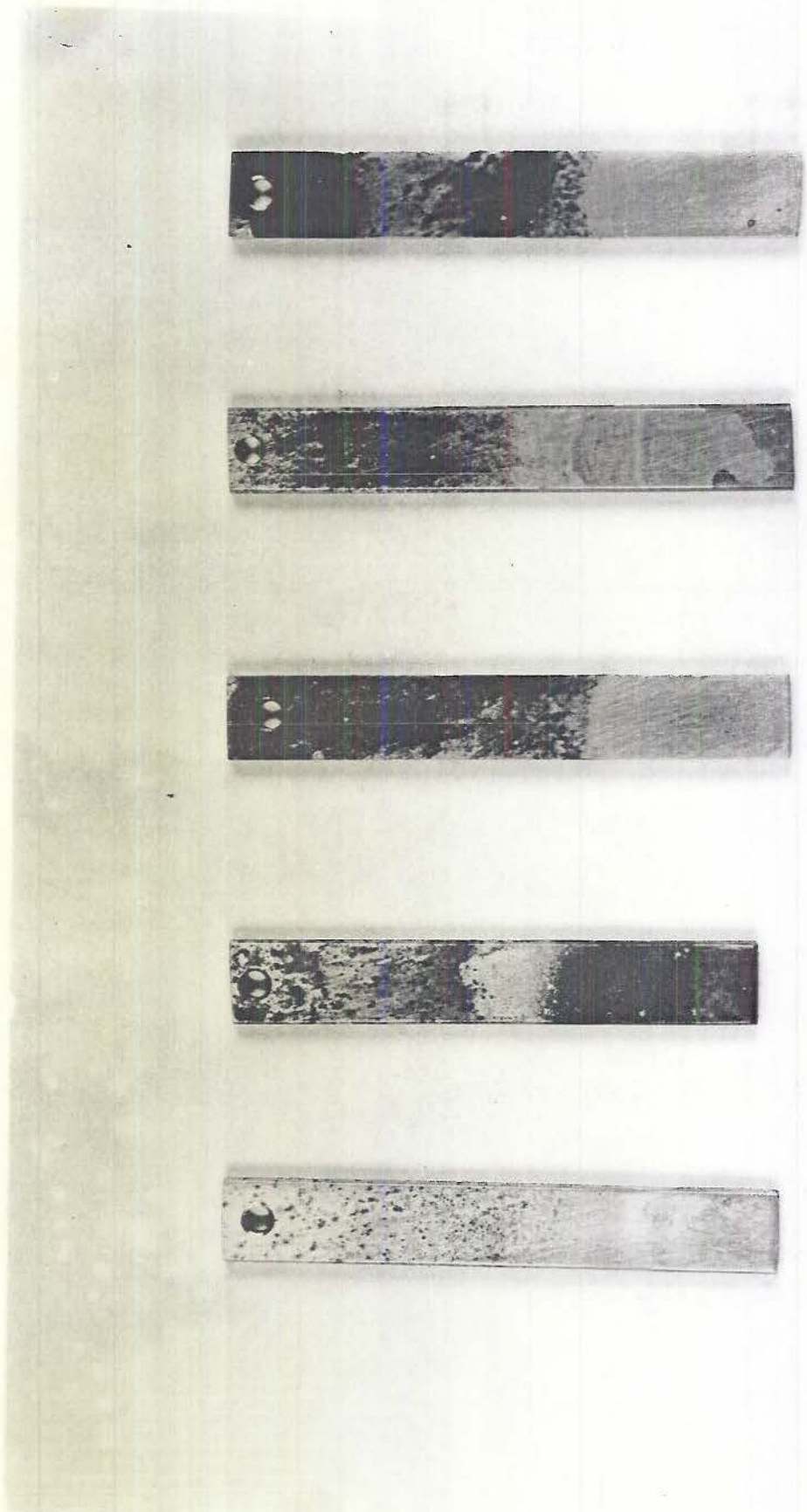
D



E

4 HRS

100°C



A B C D E



E



D



C



B



A



F

E

D

C

B

A

APPARATUS FOR CONSTANT TEMPERATURE
HEAT TREATMENT OF HALOWAX

