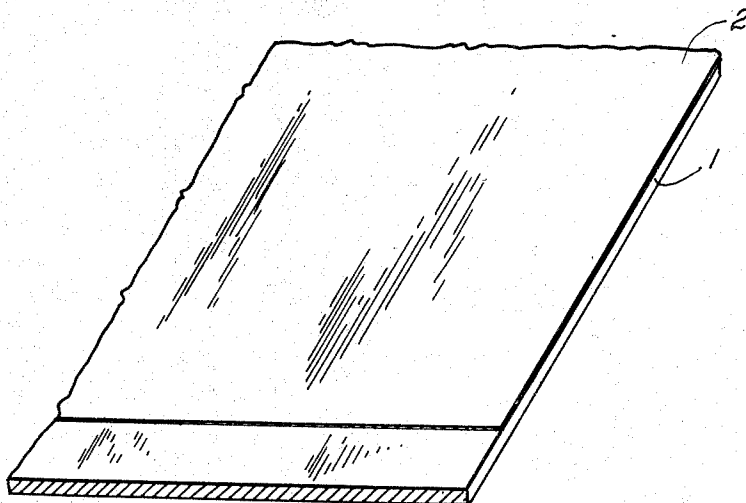


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RESINOUS COMPOSITION METHOD OF COATING METALS THEREWITH
TO INCREASE HIGH-TEMPERATURE RESISTANCE THEREOF
AND ARTICLE PRODUCED THEREBY
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1

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RESINOUS COMPOSITION METHOD OF COATING METALS THEREWITH TO INCREASE HIGH-TEMPERATURE RESISTANCE THEREOF AND ARTICLE PRODUCED THEREBY

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This invention relates as indicated to a new and useful method for improving the resistance of metal to extremely high temperatures and particularly such temperatures which are sufficient to cause the metal to fuse. More particularly, this invention is directed to the method of producing an expendable or "one shot" article which article is to be subjected for short periods of time to temperatures generally well in excess of the melting point of the metal from which the article is manufactured.

Expendable or "one shot" devices are rapidly assuming a role of ever-increasing importance, particularly from a military standpoint, and especially in the field of rockets and jet-assisted take-off tubes. Normally, devices such as these are used only once, no attempt being made to recover the shell or casing after the initial firing. In many cases the cost of the device and the weight of the device are important factors particularly where aircraft are involved. It has been found desirable to construct such devices from light metals such as aluminum, magnesium, various alloys of aluminum and magnesium, and in other cases out of the usual heavy metals but where the thickness of the metal is so reduced as to make them much lighter in weight.

This attempt at reduction of the weight of such devices has largely met with failure because of the fact that the metals sought to be employed either had too low a melting point to withstand the temperatures of the explosive or propulsive charges, or the metal was too thin to withstand the temperatures employed for a period of time sufficient for the explosive or propulsive charge to become expended. Many attempts to solve this problem by coating the metal article with various plastic compositions have met with failure.

It is a primary object of this invention, therefore, to provide a method for improving the resistance of metals to temperatures sufficient to soften the metal whereby a life of the article involved is obtained such that an explosive or propulsive charge may be expended entirely before disintegration of the metal occurs.

Another object of this invention is to provide a liquid coating composition which is suitable for use as a coating for metals which are to be subjected to temperatures generally in excess of the softening point of the metal.

Another object of this invention is to provide a convenient and inexpensive method for prolonging the time during which a metal may be exposed to temperatures in excess of the melting point of such metal.

Other objects of this invention will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention, then, consists of the means hereinafter fully described and particularly pointed out in the appended claims, the following description setting forth in detail certain illustrative embodiments of the invention, such disclosed means constituting, however, but a few of the various forms in which the principle of this invention may be employed.

In the adaptations of this invention which are of primary importance, the increased time of resistance to temperatures in excess of melting point of the metal need only be a matter of a few seconds. It will be understood, of course, that increasing thickness of the metal itself will improve the time during which the article can withstand temperatures in excess of the melting point provided, however, that those temperatures are not so greatly in excess of the melting point at reason-

2

able thicknesses and variations thereof play a minor role in the service life of the article. It is possible, therefore, to obtain correlatable and indicative results by testing the effectiveness of this invention with panels of various metals such as aluminum, magnesium, alloys of aluminum and magnesium, iron, steel, and various other alloys of iron. Tin and tin-plated articles may also be protected in accordance with this invention. An interesting example of an embodiment of this invention may be demonstrated by the following. Aluminum melts at temperatures of from 660° C. to about 700° C. A sheet of aluminum 0.125 inch thick was exposed to the tip of an oxyacetylene flame having a temperature of approximately 5500° F. Five seconds were required for this flame to burn through the aluminum sheet. When a piece of aluminum having the same thickness and composition was treated in accordance with the method of this invention, by applying a coating 0.035 inch thick, such coating being hereinafter more particularly described, and again exposed to the same acetylene torch flame, burn through times of from 35 to 55 seconds were obtained. For certain military purposes, an increase in the time of resistance of aluminum of the foregoing thickness of from 5 to 35 or 55 seconds is considerably in excess of that which is needed to allow for expenditure of a charge contained in an aluminum article having a wall thickness of 0.125 inch.

Certain other metals, although they will not melt at the temperatures developed by the charge may lose temper, and protection in accordance herewith is valuable in preserving such properties for a longer period of time.

Another requirement of the articles of this invention is that they be able to withstand impact without destroying the continuity of the coating. Therefore a method which provides an article having a flexible coating thereon is another object of this invention.

In another adaptation of this invention, articles which have heretofore been "one shot" items may be converted to "multi-shot" articles since under certain conditions only the coating would be destroyed and the shell available for recoating with the compositions hereof.

It has been found that an aqueous coating composition characterized by the presence therein of an aqueous resin emulsion of the vinyl or vinylidene halide type, an alkali metal silicate and a powdered siliceous material, is applied to the surface of the metal most nearly in contact with the heat source, allowed to dry, either by exposure to air or by force drying methods, and then exposing the coated metal to temperatures sufficient to soften the metal yields a result which is exceedingly beneficial in the rocket propulsion field.

Broadly stated, therefore, this invention comprises the provision of a composition and method for improving the resistance of metal to temperatures sufficient to soften said metal which comprises coating said metal with a liquid coating composition containing as essential ingredients:

- from about 10 parts to about 30 parts by weight of an aqueous resin emulsion of 40% to 60% solids concentration, said resin being selected from the group consisting of vinylidene halide polymers and copolymers; and vinyl halide polymers and copolymers;
- from about 15 parts to about 45 parts of a powdered siliceous material having a particle size from about 100 mesh to about 400 mesh; and
- from about 50 parts to about 75 parts of a 20% to 45% aqueous solution of an alkali metal silicate having a silica/alkali oxide ratio of from about 2.6 to about 3.4.

and drying said coating.

THE AQUEOUS RESIN EMULSION

In general, the resins which are useful in accordance with this invention are in the form of an aqueous emulsion. Not all aqueous resin emulsions are suitable for use in accordance herewith and to achieve the best results of this invention use is made of internally plasticized resins which are characterized in that they yield non-combustible decomposition products. Such resins include the polyvinylidene halide polymers and copolymers and the vinyl halide polymers and copolymers. A

preferred class of resins for use in accordance with this invention comprise those having as a base a resin prepared by the polymerization of a monomeric material comprising a haloethylene compound having from 1 to 2 halogen atoms on no more than 1 of the carbon atoms. These may be prepared by dispersing the solid finely divided polymer in water, or by polymerizing the monomeric material in aqueous emulsion. More specifically, the aqueous emulsions may be prepared by polymerizing in aqueous emulsion vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, mixtures of these materials with each other, or mixtures of one or more of these materials with other monomers co-polymerizable therewith in aqueous emulsions such as the vinyl esters of low molecular weight aliphatic acids such as vinyl acetate, vinyl propionate, vinyl butyrate, and the alkyl esters of acrylic and methacrylic acids such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, methyl ethacrylate, maleic acid or anhydride, esters of maleic acid or of chloro maleic acid, and other similar materials. Particularly preferred are the aqueous emulsions prepared by polymerization in aqueous emulsion of vinyl chloride, vinylidene chloride, mixtures of these two materials with each other, or mixtures of one or both of these materials with a lesser proportion of an alkyl ester of an alpha-methylene aliphatic mono-carboxylic acid. Examples of the latter are the alkyl esters of acrylic or methacrylic acid or the like. While it is preferred to use the well-known volatile esters of lower alcohols such as methylacrylate, ethylacrylate, methylacrylate, and the like, other esters of acrylic acid such as butyl acrylate, dodecyl acrylate, phenyl acrylate, ethylene diacrylate, and the like may also be used. A preferred class of resins consists of those made from monomeric materials in which the chloro-ethylene is the predominant constituent, that is, amounts to more than 50% by weight of the material. Complete instructions concerning the preparation of these vinyl resin emulsions may be found in U. S. Patent 2,431,745.

In general, the vinyl resin emulsions contain 40 to 60% solids and are employed in the compositions of this invention in amounts ranging from 10% to 30% by weight of the composition. It is an important criterion of the aqueous emulsion resins that they be stable under fairly strong alkaline conditions. Experience has indicated that polymers and co-polymers of halide-free monomers when the halide-free monomer was in the major amount, are generally unsuited for use in accordance with this invention. Thus, rubber latices, styrene-butadiene latices, and the like are not satisfactory for these purposes.

It has been found that the aqueous emulsion utilized in accordance with this invention impart an impact resistance to the coating composition when applied as a film over the metal. However, there is another distinct advantage of this particular class of emulsion resins and that is to provide under firing conditions a decomposable material, the decomposition products of which are essentially non-combustible which in the presence of the remaining essential ingredients of the composition in the fused state cause intumescence or the production of voids within the fused mass.

THE SILICEOUS COMPONENT

The siliceous materials suitable for use in accordance with the present invention are generally of the inactive type. Specific examples of such siliceous materials include Georgia kaolin, china clay, bentonite, diatomaceous silica, perlite, and the like. These materials in combination with the alkali silicate are capable of forming a fusible mass and in further combination with the latex forms an intumesced porous mass serving as an insulating film from the high temperatures. Another function of the siliceous component is to provide a reinforcing pigment for the silicate which in the absence of the siliceous component would provide an entirely unsatisfactory film due to cracking and spawling. It has also been found that inclusion of the siliceous component in these compositions aids in the release of water when the composition is drying. Thus, it is preferred that the siliceous component employed in these compositions, while easily dispersible in water, should not have too great a water adsorptive power. Bentonite, while it may be used, nevertheless produces a less satisfactory product. A preferred example of siliceous material is perlite in the expanded or unexpanded form. This material provides a

much faster release of water and may be used as a replacement of part or all of other clay components such as Georgia kaolin or diatomaceous silica. Perlite also aids in producing a composition which is much more suited to spray application. Perlite is a volcanic glass.

In general, the amount of siliceous material employed is from about 15 to 45 parts per 100 parts of composition.

THE ALKALI METAL SILICATE

The alkali metal silicate used in accordance with this invention is employed as an aqueous solution containing from 25 to 45% alkali metal silicate. Generally the commercially available sodium silicate having a silica ratio of from 2.5 to about 3.4 and available as approximately 38% solutions may be used. Sodium silicate, potassium silicate or lithium silicate may be employed with sodium silicate being preferred because of its ready availability and low cost. In general from 50 parts to 75 parts per 100 parts of coating composition of the commercial approximately 38% solution is employed. If the viscosity of the resulting composition is too high it has been found convenient to add up to 10% by weight of water to adjust the viscosity to a suitable brushing or spraying consistency.

The foregoing materials may be combined by simple mixing, but it is preferred to pass the composition through a paint mill.

It becomes convenient at this point to illustrate the manner in which compositions suitable for use in accordance herewith may be formulated by giving a few specific examples which are to be understood as illustrative only and not to be construed as limiting the invention to the precise scope thereof.

Example I

301 lbs. of Georgia kaolin clay were mixed with 55.5 gallons of a sodium silicate solution having a sodium oxide to silicon dioxide ratio of 1:3.22 and a specific gravity of 41.0% Baumé. This mixture was passed rapidly through a roller mill and to the milled mixture were added 29.25 gallons of a polyvinylidene chloride-polyvinyl chloride co-polymer containing a small amount of an alkyl ester of an alpha methylene aliphatic monocarboxylic acid such as methyl methacrylate. This resin emulsion had a solids content of 50%. The resulting composition was then ready for use in coating expendable metal objects.

Example II

326 lbs. of Georgia kaolin clay, 71 lbs. of diatomaceous silica, 50.5 gallons of a potassium silicate solution having a potassium oxide to silicon dioxide ratio of 1:3.29 and a specific gravity of 40.75° Baumé, and 15 gallons of water were mixed together and passed through a roller mill. This composition was then blended with 7 gallons of water and 10 gallons of an aqueous emulsion having a solids content of 50% of a polyvinylidene chloride-polyvinyl chloride co-polymer such as used in Example I above. This composition was then ready for use in coating expendable metal objects.

Example III

300 lbs. of perlite (volcanic glass), 70 lbs. of Georgia kaolin clay and 51.5 gallons of a sodium silicate solution having a sodium oxide to silicon dioxide ratio of 1:3.22 and a specific gravity of 41.0° Baumé were mixed and ground for 4 hours in a pebble mill and then blended with 23 gallons of an emulsion having a solids content of 50%, the resinous component of said aqueous emulsion being a polyvinylidene chloride-polyvinyl chloride resin. This composition was then ready for use in accordance with this invention.

Other examples may be formulated in accordance with the instructions illustrated above to provide further compositions which are useful in accordance herewith. The foregoing examples show compositions which contain a vinylidene halide resin emulsion in amounts ranging from about 9.5% or 10% to about 30% by weight of the composition when calculated as a 50% solids solution. The siliceous material as exemplified by kaolin and diatomaceous silica may be employed in amounts ranging from about 15 to about 45% by weight of the entire composition. The alkali metal silicate component in the foregoing examples was an approximately 38% solution and as such may account for anywhere from 50 to 75% by weight of the entire composition. Mixed siliceous ma-

terials may be employed as illustrated in Example II. While sodium silicate is a convenient alkali metal silicate for use in accordance herewith, potassium silicate or lithium silicate solutions may also be employed. Lithium silicate solutions are, however, impractical from a commercial point of view.

The compositions of this invention may be applied conveniently by spray, brush, or dip methods, to provide a film which is preferably from 0.02 to 0.06 inch thick. These films may be air dried, but for best results it has been found that force drying at a temperature not exceeding about 210° F. for a period of 45 minutes to 1 hour is to be desired. If higher temperatures for drying are employed, certain latices may tend to fuse and form a film over the surface before the water is completely expelled. Too low temperatures for drying do not appear to give satisfactory water release.

The compositions of this invention when dried as films are completely water-soluble. An additional ingredient, such as wax or a silicone resin, may be incorporated in the coating compositions to improve the water resistance of the film. Other methods of insolubilizing alkali silicate films are well known, such as acid or acid salt treatment. The water sensitive films may also be protected by the use of a lacquer or latex emulsion top coating which may or may not be pigmented, such as for identification purposes.

The annexed drawing is a fragmentary isometric view of an article produced in accordance with this invention, having a base metal 1, such as aluminum, and a film 2 applied thereover and formed from one of the compositions of this invention.

Other modes of applying the principle of this invention may be employed instead of those specifically set forth above, changes being made as regards the details herein disclosed, provided the elements set forth in any of the following claims, or the equivalent of such be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. The method for improving the resistance of metal to temperatures sufficient to soften said metal which comprises coating said metal with a liquid coating composition containing as essential ingredients: (a) from about 10 parts to about 30 parts by weight of an aqueous resin emulsion of 40% to 60% solids concentration; said resin being selected from the group consisting of vinylidene halide polymers and co-polymers and vinyl halide polymers and co-polymers; (b) from about 15 parts to about 45 parts of a powdered siliceous material having a particle size of from about 100 mesh to 400 mesh, and (c) from about 50 parts to about 75 parts of a 20% to 45% aqueous solution of an alkali metal silicate having a silica/alkali oxide ratio of from about 2.6 to about 3.4 and drying said coating.

2. The method for improving the resistance of metal having melting points in the range of from about 500° C. to about 1500° C. to temperatures sufficient to soften said metal which comprises coating said metal with a liquid coating composition containing as essential ingredients: (a) from about 10 parts to about 30 parts by

weight of an aqueous resin emulsion of 40% to 60% solids concentration, said resin being selected from the group consisting of vinylidene halide polymers and co-polymers and vinyl halide polymers and co-polymers; (b) from about 15 parts to about 45 parts of a powdered siliceous material having a particle size of from about 100 mesh to 400 mesh, and (c) from about 50 parts to about 75 parts of a 20% to 45% aqueous solution of an alkali metal silicate having a silica/alkali oxide ratio of from about 2.6 to about 3.4 and drying said coating.

3. The method of improving the resistance of aluminum to temperatures sufficient to soften the aluminum which comprises coating the aluminum with a liquid coating composition containing as essential ingredients: (a) from about 10 parts to about 30 parts by weight of an aqueous resin emulsion of 40% to 60% solids concentration; said resin being selected from the group consisting of vinylidene halide polymers and co-polymers and vinyl halide polymers and co-polymers; (b) from about 15 parts to about 45 parts of a powdered siliceous material having a particle size of from about 100 mesh to 400 mesh, and (c) from about 50 parts to about 75 parts of a 20% to 45% aqueous solution of an alkali metal silicate having a silica/alkali oxide ratio of from about 2.6 to about 3.4 and drying said coating.

4. As an article of manufacture aluminum coated with the composition described in claim 1.

5. The method for improving the resistance of magnesium-containing metals to temperatures sufficient to soften said metal which comprises coating said metal with a liquid coating composition containing as essential ingredients: (a) from about 10 parts to about 30 parts by weight of an aqueous resin emulsion of 40% to 60% solids concentration; said resin being selected from the group consisting of vinylidene halide polymers and co-polymers and vinyl halide polymers and co-polymers; (b) from about 15 parts to about 45 parts of a powdered siliceous material having a particle size of from about 100 mesh to 400 mesh, and (c) from about 50 parts to about 75 parts of a 20% to 45% aqueous solution of an alkali metal silicate having a silica/alkali oxide ratio of from about 2.6 to about 3.4, and drying said coating.

6. A coating composition for improving the resistance of metal to temperatures sufficient to soften the metal comprising: (a) from about 10 parts to about 30 parts by weight of an aqueous resin emulsion of 40% to 60% solids concentration; said resin being selected from the group consisting of vinylidene halide polymers and co-polymers and vinyl halide polymers and co-polymers; (b) from about 15 parts to about 45 parts of a powdered siliceous material having a particle size of from about 100 mesh to 400 mesh, and (c) from about 50 parts to about 75 parts of a 20% to 45% aqueous solution of an alkali metal silicate having a silica/alkali oxide ratio of from about 2.6 to about 3.4.

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