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METHOD OF MASKING A SURFACE WITH A SALT OF A CARBOXYLIC ACID AND AN AMINOALKANE PRIOR TO DYEING

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This invention relates to a novel method of masking a surface to protect the same against coloring during subsequent dyeing of an adjoining surface.

A simplified flow diagram of one embodiment of the process of the present invention is as follows:

↓

Polish

↓

Anodize

↓

Mask with carboxylic acid-aminoalkane salt

↓

Dye

↓

Remove masking

↓

Referring to the flow diagram, the metal article is polished in all or in part and then is subjected to anodizing in the manner to be hereinafter described in detail. The portion of the metal article to be protected against coloring is then coated with the masking material of the present invention, following which the metal article is subjected to a dyeing treatment. Following the dyeing treatment, the masking material is removed by means of a suitable solvent as hereinafter set forth. Intervening and final rinsing and drying steps have been omitted from the drawing in the interest of simplicity but will be provided as required.

In numerous cases it is desired to color only a portion of an object and either leave the remaining portion uncolored or to dye the same a different color. In other cases it is desired to apply three or more different color schemes to the same article. In still other cases, it is desired to imprint an emblem, insignia, wording, numerals or the like on an article of manufacture and to leave the remaining portion of the article uncolored or to apply one or more different colors thereto. In the past, it has been the general practice to cover the portion of the surface to be protected with masking tape, then apply the coloring material to the unprotected surfaces and finally remove the masking tape. In still other cases, where the articles to be colored are of conical, elliptical, parabolic, dished, box or other shape and are hollow inside, one method is to tightly bind two of these articles together at the fronts thereof and then apply a dyeing treatment to the exposed surfaces. It is readily apparent that these methods are both time consuming and leave much to be desired. The present invention is directed to a novel method of masking the surfaces to be protected and to thereby considerably facilitate the desired dyeing treatment.

The present invention is particularly applicable for use in the coloring of metal surfaces. One outstanding use is in connection with the treatment of reflectors used in

street lights, vehicle lights, photographic equipment, etc. These reflectors preferably are made of aluminum or aluminum alloy and during their treatment are subjected to an anodizing step. However, before such anodizing the inner surface of the reflector is polished to give the desired mirror effect. Because in many cases these reflectors are not encased in a housing, it also is necessary to color the back of the reflector for obvious esthetic reasons. However, it is essential that the polished inner surfaces are not contaminated during the dyeing operation. In the past it has been the practice to tightly bind two of the reflectors together and then dye the backs thereof. In accordance with the present invention, a novel liquid masking material is applied to the polished inner surface and this serves to protect the polished surface during the dyeing treatment.

Another outstanding use of the present invention is in the dyeing of metal strips, shapes, ornaments, designs, etc. used in industrial machinery, vehicles including automobiles, trucks, tractors, etc., boats, airplanes, household appliances, such as handles, trim, or ornaments for refrigerators, toasters, rotisseries, broilers, etc. In many cases it is desired either to use different color schemes on the same or adjoining surfaces or to imprint a trade name, number or other identifying mark thereon. In accordance with the present invention, the novel liquid masking material is applied to the surface to be protected, and the article then is subjected to the dyeing treatment, after which the liquid masking material is removed, and the protected surface either is left as is or is dyed a different color.

From the above general description, it will be seen that the novel process of the present invention may be used in the coloring of ferrous metals, non-ferrous metals and alloys thereof including, for example, iron, steel, copper, brass, bronze, nickel, aluminum, etc. In another embodiment, the present invention may be used in the coloring of other solid surfaces including those made of glass, ceramic, wood, rubber, plastic, etc. As hereinbefore set forth, the present invention is particularly useful in the coloring of aluminum and alloys thereof, which are subjected to a subsequent dyeing and sealing treatment. Numerous lacquers were evaluated and found to be unsatisfactory for this purpose.

In one embodiment the present invention relates to a method of masking a surface to protect the same against coloring during subsequent dyeing of an adjoining surface, which comprises first applying to the surface to be protected a coating material comprising a salt of a carboxylic acid and an aminoalkane, then subjecting said adjoining surface to a coloring treatment, and subsequently removing said salt from said first-mentioned surface.

As hereinbefore set forth, the surface to be protected may comprise a portion of a larger surface or it may comprise a full surface adjoining other surfaces. Examples of the latter surface are the top and/or bottom of a box, drum or other container, one side of an angle beam, the face of a filing cabinet, etc. It is understood that reference to surface in the present specification and claims is intended to include both a portion of a larger surface or a full surface adjoining other surfaces.

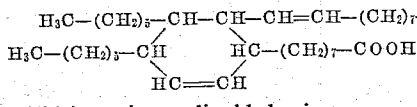
In accordance with the present invention, the surface to be protected is covered with a masking liquid comprising a salt of a carboxylic acid and an aminoalkane. Any suitable carboxylic acid may be utilized in forming the salt. In a preferred embodiment the carboxylic acid comprises a polybasic carboxylic acid. While the polybasic carboxylic acid may comprise oxalic, malonic, succinic, glutaric, itaconic, mesaconic, citraconic, et., it preferably contains at least 6 carbon atoms, referred to herein as high molecular weight carboxylic acid, and thus in-

cludes adipic, pimelic, suberic, azelaic, sebacic, phthalic, etc., aconitic citric, etc., hemimellitic, trimesic, prehnitic, mellophanic, pyromellitic, mellitic, etc., and higher molecular polybasic carboxylic acids.

In a particularly preferred embodiment, the polybasic acid contains at least 10 carbon atoms per molecule and more particularly from about 20 to about 50 carbon atoms per molecule. An especially preferred acid comprises a mixed by-product acid being marketed commercially under the trade name of "VR–1 Acid." This is an acid residue produced by distilling, at about 270° C. under about 4 mm. of mercury pressure, the by-product acids obtained in the preparation of sebacic acid by fusing castor oil with alkali. Production of this residue is described in more detail in U.S. Patent 2,267,269 to Cheetham et al. In the manufacture of sebacic acid from castor oil, the oil is heated with a caustic alkali. This splits the oil, forming octanol-2, methyl hexyl ketone, the alkali salt of sebacic acid, and the alkali salts of various other long-chained acids. The alcohol and ketone are readily removed from the reaction mixture by distillation. The alkali salts which remain then are dissolved in water and, upon slight acidification of the resulting solution, an oily layer separates. At a pH of about 6, the aqueous phase contains the alkali salt of sebacic acid, while the oily layer contains various other acids from the reaction. the term "by-product acids" is generally applied to the mixture of acids forming the oily layer.

These by-product acids then are separated into two parts. After these acids have been washed with a dilute mineral acid, such as sulfuric or hydrochloric, they are washed with water and dried. They then are distilled under reduced pressure. Fatty acids which are primarily monobasic carboxylic acids are taken off at 100° C. to 270° C. at pressures as low as 4 mm. This treatment leaves a residue which is a mixture of fatty acids, apparently primarily polybasic in character. The residue is commercially available from Rohm & Haas Company under the trade name of VR–1 Acid and has an average molecular weight of 500–600, an acid number of 134–160, a saponification number of 174–179, and an iodine number of 53–60.

Another mixed by-product acid is being marketed commercially under the trade name of "Dimer Acid." Still another preferred acid is marketed commercially under the trade name of "Empol 1022." This dimer acid is a dilinoleic acid and is represented by the following general formula:



This acid is a viscous liquid, having an apparent molecular weight of approximately 600. It has an acid value of 180–192, an iodine value of 80–95, a saponification value of 185–195, a neutralization equivalent of 290–310, a refractive index at 25° C. of 1.4919, a specific gravity at 15.5° C./15.5° C. of 0.95, a flash point of 530° F., a fire point of 600° F., and a viscosity at 100° C. of 100 centistokes.

Other dicarboxylic acids containing at least 10 carbon atoms per molecule include alkyl substituted acids having the desired number of carbon atoms in the alkyl group. Illustrative acids include alkyl malonic acid, alkyl succinic acid, alkyl glutaric acid, alkyl adipic acid, alkyl pimelic acid, alkyl suberic acid, alkyl azelaic acid, alkyl sebacic acid, alkyl phthalic acid, and higher molecular weight dicarboxylic acids. A particularly preferred acid in this class is dodecyl succinic acid.

While the dicarboxylic acids are particularly preferred, it is understood that monocarboxylic acids may be used and particularly those containing at least 6 and preferably at least 10 carbon atoms per molecule. Illustrative acids in this class include caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachidic, behenic, cerotic, etc., decylenic, palmitoleic, oleic, ricinoleic, linoleic, linolenic, etc.

Any suitable aminoalkane may be utilized in forming the salt. Here again it is preferred that a diaminoalkane having at least 6 and preferably at least 10 carbon atoms per molecule be used. Conveniently a major portion of the carbon atoms is present in the form of an alkyl substituent as, for example, in such compounds as

N-alkyldiaminoethane,
N-alkyl-1,3-diaminopropane,
N-alkyl-1,3-diaminobutane,
N-alkyl-1,4-diaminobutane, etc.,

in which the alkyl group contains at least 4 carbon atoms and preferably from about 10 to about 40 carbon atoms. Illustrative preferred N-alkyl-1,3-diaminopropanes include

N-dodecyl-1,3-diaminopropane,
N-tridecyl-1,3-diaminopropane,
N-tetradecyl-1,3-diaminopropane,
N-pentadecyl-1,3-diaminopropane,
N-hexadecyl-1,3-diaminopropane,
N-heptadecyl-1,3-diaminopropane,
N-octadecyl-1,3-diaminopropane,
N-nonadecyl-1,3-diaminopropane,
N-eicosyl-1,3-diaminopropane,
N-heneicosyl-1,3-diaminopropane,
N-docosyl-1,3-diaminopropane,
N-tricosyl-1,3-diaminopropane,
N-tetracosyl-1,3-diaminopropane,
N-pentacosyl-1,3-diaminopropane,
N-hexacosyl-1,3-diaminopropane,
N-heptacosyl-1,3-diaminopropane,
N-octacosyl-1,3-diaminopropane,
N-nonacosyl-1,3-diaminopropane,
N-triacontyl-1,3-diaminopropane,
N-hentriacontyl-1,3-diaminopropane,
N-dotriacontyl-1,3-diaminopropane,
N-tritriacontyl-1,3-diaminopropane,
N-tetratriacontyl-1,3-diaminopropane,
N-pentatriacontyl-1,3-diaminopropane, etc.

A particularly preferred N-alkyl-1,3-diaminopropane is commercially available under the trade name of "Duomeen-T." Other N-alkyl-1,3-diaminopropanes comprise those in which the alkyl group is derived from lauric acid, coconut oil, soya oil, etc. These N-alkyl-1,3-diaminopropanes are available commercially at the present time and comprise mixed alkyl-substituted 1,3-diaminopropanes. For example, in the case of "Duomeen-T," the alkyl substituent contains from about 12 to about 20 carbon atoms per group and mostly containing 16 to 18 carbon atoms.

While the N-alkyl-diaminoalkanes and particularly N-alkyl-1,3-diaminopropanes are particularly preferred, in some cases the monoamine may be employed and, here again, preferably contains at least 6 and still more particularly at least 10 carbon atoms per molecule. Illustrative monoamines includes decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexadecylamine, heptadecylamine, octadecylamine, nonadecylamine, eicosylamine, heneicosylamine, docosylamine, tricosylamine, tetracosylamine, pentacosylamine, etc. Many of these amines are derived from the corresponding fatty acids and are identified accordingly as, for example, lauryl amine, stearic amine, etc.

It is understood that a mixture of the amines and/or acids may be employed and that they will be selected to produce the desired salt. For example, when an acid of comparatively low molecular weight is utilized, the amine preferably contains a larger number of carbon atoms per molecule. Similarly, when the amine contains a comparatively low number of carbon atoms per molecule, the acid employed contains a comparatively high number of atoms per molecule. Also it is understood

that the various acids and amines are not necessarily equivalent for use in the various applications.

In general, the acid salt of the polybasic acid and polyamine is preferred. The acid salt is prepared by utilizing a stoichiometric excess of acid with relation to the amine as, for example, two equivalents of acid per one equivalent of amine. In another embodiment, the salt may be a neutral salt, which is prepared by utilizing stoichiometric amounts of acid and amine. In other words, the concentration of polybasic acid and polyamine will be selected so that there will be an equivalent number of carboxylic acid groups to amino groups. Thus, the specific concentrations will depend upon whether the acid is monobasic, dibasic, tribasic or higher polybasic acid, and whether the amine is monoamine, diamine, triamine or higher polyamine. In another embodiment, the salt may be a basic salt, which is prepared by utilizing a deficiency of carboxylic acid groups in relation to the amino groups as, for example, by utilizing one equivalent of carboxylic acid per two equivalents of amine. It is understood that these different salts are not necessarily equivalent.

The salt may be prepared in any suitable manner and, in general, is readily prepared by admixing the polybasic acid and polyamine at ambient temperature, preferably with vigorous stirring. The salt is readily prepared at room temperature, although slightly elevated temperature which generally will not exceed about 200° F. may be employed when desired. Excessive temperature should not be permitted because of the undesired formation of polyamides or other reaction products. In some cases, it is desirable to utilize a solvent, either in forming a more fluid mixture of the acid and/or amine before mixing, or during the mixing thereof. In most cases it is desirable to admix the salt with a solvent in order to form a final product having the desired properties for the particular application. Particularly preferred solvents comprise hydrocarbon distillates including naphtha, kerosene, lube oil, etc., or aromatic hydrocarbons including benzene, toluene, ethylbenzene, cumene, decalin, etc. As hereinbefore set forth, when a solvent is used, the solution is prepared to produce a final product of the desired physical properties and may contain from about 10% to about 70% by weight of solvent. A particularly preferred composition contains from 20% to 60% by weight of the solvent.

As hereinbefore set forth, the salt prepared in the above manner is applied to the surface to be protected prior to the dyeing treatment. The salt may be applied to the surface in any suitable manner, such as by painting, brushing, spraying, partial dipping, etc., and will be applied in a sufficient amount to adequately protect the surface. Generally, a thin film of the salt is sufficient, although this may be varied to any desired thickness. Subsequent to the dyeing treatment, the masking material is removed in any suitable manner. In one method the salt is removed by means of a suitable solvent including benzene, toluene, naphtha, trichloroethylene, methyl isobutyl ketone, isophorone, etc. It has been found that the salt is readily removed in this manner and, as hereinbefore set forth, serves to protect the polished inner surface of reflectors during the subsequent dyeing and sealing operation.

As hereinbefore set forth, the features of the present invention are particularly useful in the coloring of aluminum products. In the manufacture of reflectors, the inner surface is polished and then the reflectors are subjected to anodizing. The anodizing may be effected in any suitable manner, including the use of sulfuric acid, which may vary from 5% to 70% concentration but preferably is from 10 to 20%, a temperature within the range of from about 20° to about 35° C., utilizing a current density of from about 10 to 50 and preferably 10 to 20 amperes per square foot, and a voltage varying from 25 to 30 volts at the beginning of operation and increasing to a maximum of from 40 to 60 volts during the course of the operation. Following the anodizing, the backs of the reflectors are coated with the salt of the carboxylic acid and aminoalkane as hereinbefore set forth, and the reflectors then are dyed and sealed in either simultaneous or successive treatments. General practice is to dye and seal in a single operation, and in this case the reflectors are dipped in hot water containing the dye. Any suitable dye may be used including those conventionally available under the trade names of Fast Acid Violet ARR, Neolan Blue 2G, Neolan Green BL, Oxanol Gold S, Oxanol Red BL, Oxanol Green BA, Rocceline, etc. The simultaneous dyeing and sealing may be effected at a temperature of from about 70° to about 100° C. for a period of from about 5 to about 30 minutes. When these operations are effected separately, the dyeing operation precedes the sealing operation and both of these operations are effected at about the same temperature and for the same length of time as hereinbefore set forth for the simultaneous operation. In some cases, when the dyeing and sealing are done separately, it may be desirable to remove the masking material after the dyeing but before the sealing treatment.

The following examples are introduced to illustrate further the novelty and utility of the present invention but not with the intention of unduly limiting the same.

Example I

The inner surfaces of a number of aluminum reflectors, suitable for use in street lighting, were polished in the conventional manner. The reflectors then were anodized with a 15% sulfuric acid electrolyte, 12 amperes per square foot current and a temperature of 35° C. for about 12 minutes.

The masking material of this example is the salt of VR–1 Acid of N-tallow-1,3-diaminopropane. The properties of the acid and amine have been described heretofore. The specific salt was an acid salt and was prepared by moderately warming 384 parts by weight of Duomeen-T and then gradually adding thereto 1542 parts by weight of VR–1 acid with vigorous stirring. Sufficient naphtha was added to the resultant salt to prepare a 40% by weight solution thereof.

The salt prepared in the above manner was utilized as a masking liquid in the anodized reflectors described above. The salt was brushed onto the inner surfaces of the reflectors and then the reflectors were dyed and sealed by being placed in a conventional dye solution at a temperature of 98° C. for about 15 minutes. The reflectors were removed from the dye and washed with benzene to remove the masking material. It was found that the polished inner surfaces were uncolored, while the backs of the reflectors were satisfactorily dyed.

Example II

An aluminum strip, 36″ x 3″ x ⅛″ is prepared with an insignia of different color in the center of the strip. This strip is used as trim and the insignia enhances its decorative effect. The masking material used in this example is the neutral salt of the Empol 1022 acid and lauryl amine. It is prepared by mixing, with vigorous stirring, the acid and amine in stoichiometric amounts. The product is recovered as a viscous liquid and is used without dilution.

A stencil of the insignia is placed on the center of the strip and the salt prepared in the above manner is painted thereon. The strip then is subjected to sealing and dyeing in the manner hereinbefore set forth. The strip is removed from the dye vat and subsequently the masking material is removed by washing with trichloroethylene.

I claim as my invention:

1. A method of masking a surface to protect the same against coloring during subsequent dyeing of an adjoining surface, which comprises first applying to the surface to be protected a coating material comprising a salt of a carboxylic acid and an aminoalkane, then subjecting said adjoin-

ing surface to a coloring treatment, and subsequently removing said salt from said first mentioned surface.

2. The method of claim 1 further characterized in that said salt is a salt of a dicarboxylic acid having at least 10 carbon atoms and an N-alkyl-1,3-diaminopropane having an alkyl group of at least 12 carbon atoms.

3. The process of claim 2 further characterized in that said alkyl group is derived from tallow.

4. The process of claim 2 further characterized in that said alkyl group is derived from lauric acid.

5. The process of claim 2 further characterized in that said alkyl group is derived from coconut oil.

6. The proces of claim 2 further characterized in that said alkyl group is derived from soya oil.

7. A method of making a surface of an aluminum article to protect the same against coloring during subsequent dyeing of an adjoining surface, which comprises first applying to the surface to be protected a coating material comprising a salt of a dicarboxylic acid having at least 10 carbon atoms and an N-alkyl-1,3-diaminopropane having an alkyl group of at least 10 carbon atoms, then subjecting said adjoining surface to a coloring treatment, and

subsequently removing said salt from said first mentioned surface.

8. The method which comprises polishing the inner surface of an aluminum reflector, anodizing the reflector, applying to the polished inner surface a coating material comprising a salt of a dicarboxylic acid having at least 10 carbon atoms and an N-alkyl-1,3-diaminopropane having an alkyl group of at least 10 carbon atoms, then subjecting said reflector to a dyeing treatment and thereby coloring the unpolished surface thereof, and subsequently removing said salt from the polished inner surface.

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