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AQUEOUS DISPERSIONS OF ELECTRO-
POSITIVE MATERIALS

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This invention relates to dispersions comprising water-insoluble particles, surface active cationic material, and a coupling agent, the dispersions being substantive to textiles, paper, leather, nylon, Cellophane, and the like. The invention relates also to articles treated with the dispersions and to the method of treatment.

It is customary to treat certain articles such as textiles and thread with emulsions or dispersions, in order to lubricate, soften, oil, or wax the articles. Conventional emulsions or dispersions used for such purpose show no substantial substantivity or attraction of the dispersed particles for the articles being treated. As a result, the dispersed particles are deposited on the articles only by the absorption of the dispersions by the article and subsequent evaporation of water from the absorbed dispersion. Furthermore, the dispersions used are frequently so unstable as to undergo segregation to objectionable extent, particularly when in dilute condition.

The present invention provides dispersions that are comparatively stable and substantially non-segregating even when diluted. The invention provides, also, dispersions in which the dispersed particles are substantive to a great variety of articles to be treated and are adsorbed by the articles when treated with the dispersions. Thus, the invention provides dispersions of wax or like material that are substantive to textiles and from which textiles exhaust finally the dispersed particles, so as to leave finally practically clear water.

The invention comprises dispersions including water-insoluble, normally electropositive particles, a surface active cationic material, and a coupling agent, the coupling agent serving to improve and stabilize the dispersion, presumably largely by promoting closeness or thoroughness of association of the said dispersed particles with the cationic material, and causing the dispersed particles to remain properly associated with the cationic material as the latter is exhausted from the dispersion by a textile material or the like. The normally electropositive particles are modified by association with the cationic material and the coupling agent, so that the aggregate including the particles is electronegative and, therefore, readily adsorbed by electropositive materials such as textiles, paper, or the like. The invention comprises also the product resulting from and the method of treating articles with dispersions of the kind described so that desired impregnation of the article by the dispersions is obtained.

To make the dispersions of the present invention, there is formed an emulsion or dispersion of the said water-insoluble particles, the cationic material, and the coupling agent, usual mechani-

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cal means being employed for effecting the dispersion.

When the dispersions during use are contacted with a material such as a textile, paper, or leather, the material exhausts the dispersed particles from the dispersion. Because of the substantivity, the dispersed particles come to be distributed over the surface of the material treated and penetrate adequately within the material, exhaustion of the dispersed particles from the treating vat finally occurring when a large proportion of the material has been treated with a relatively limited proportion of the dispersion.

Cationic material

The cationic material used is an organic compound which, when dissolved in water, gives a surface active positive ion containing a substantial number of carbon atoms, say, 6 to 20.

Among the cationic materials that may be used are those that are surface active and that have a relatively large number of carbon atoms and that are compounds of the aliphatic, cyclic or heterocyclic amines with acids. The compounds are of the type of salts. Such materials include, for example, the salts of the lauric, oleic, and stearic acid amido-amines. Typical examples of such compounds are the salts of the mono-acyl derivatives of ethylene diamine, butylene diamine, and hexylene diamine, with a mineral or organic acid. The amine, which is condensed with one molecule of the fatty acid, to give the mono-amide, may be either a non-substituted or a substituted amine including hydroxyl, chlorine, or other substituent groups. In place of the amino compounds described, there may be substituted the corresponding phosphonium compounds or quaternary ammonium compounds.

The acid used to form the salts of the compounds of the class described and to produce therewith the cationic material may be formic, acetic, lactic, propionic, hydrochloric, sulfuric, and like water soluble acids of relatively low molecular weight.

The salts of these compounds, on ionizing in the presence of water, show complex organic residues having a positive charge. The positive ions given by these cationic materials are known to be surface active.

The individual reactants chosen for making the cationic material should include at least one compound containing a hydrocarbon radical of substantial size, so that the finished cationic material will contain at least 6 and preferably 10 to 20 or somewhat more carbon atoms to the molecule.

Coupling agent

The coupling agent is an organic compound that contains a hydrophilic group, is not ionized

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in water to a large extent, and does not readily form salts in dilute acids or alkalis. For best results the coupling agent should also be insoluble in water. The number of carbon atoms to the molecule of the coupling agent is relatively large, say, 6 to 20 to the molecule, so as to make the compound rather complex. The coupling agent preferably contains an acyl group. The hydrophylic group should preferably include a hydroxyl or an amide group or both.

Among the coupling agents that may be used are the following: higher fatty acid amides of acyl or hydroxyacyl amines and other fatty acid amides. In some cases, higher alcohols may be used.

The general formula for a particularly satisfactory class of coupling agents is the following:



$R-CO-$ being an acyl group, as, for example capryl, lauryl, oleyl, or stearyl, and R_1 being an alkyl group such as methyl, ethyl, butyl, octyl, or dodecyl with one hydrogen replaced by hydroxyl.

In the above type formula, NH may become NR_2 , R_2 being an alkyl group of the kind described in connection with the meaning of R_1 .

Dispersions—In general

The emulsifier (the basic compound adapted on neutralization to become the cationic material) is melted, if a solid normally, or otherwise mixed thoroughly with the coupling agent. Acid is added to neutralize a substantial portion at least and preferably practically all of the said basic material. Water is then added in amount adequate to dissolve or disperse the acid treated material uniformly, when the mixture is stirred.

The water-insoluble particles to be dispersed, in either very finely divided or melted form, are added slowly to the aqueous mixture including the cationic material and coupling agent, the mixture being stirred vigorously during the addition. If the said particles are molten, the temperature is maintained at least slightly above the melting point of the particles. The stirring is continued in any case until the mixture appears to be homogenous.

The proportions of the materials used in making the dispersions may be varied over a considerable range. Thus, the ingredients may be used in the following proportions:

Cationic material.....	2 to 15 parts
Coupling agent.....	2 to 20 parts
Dispersed particles.....	Up to 45 parts or more
Water.....	To make 100 parts

Stability of the dispersions is increased by the use of larger proportions of the cationic material and coupling agent. On the other hand, unnecessarily large proportions of these materials involve expense that may be avoided. In general, there are used the minimum (most economical) proportions of these components which give to the dispersion the stability necessary for the purpose for which the dispersion is to be used, and also the property of being substantive to the material to which the emulsion is to be applied if the emulsion is to be applied to a penetrable article.

For most purposes it is desirable to use approximately 5 to 10 parts of the cationic material and 10 to 15 parts of the coupling agent. Thus, with 6 parts of cationic material and 12 parts of coupling agent there has been made a stable

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emulsion including 45 parts of dispersed paraffin wax in 100 parts of the total emulsion.

Proportions here and elsewhere herein are expressed as parts by weight.

Dispersions made as described may undergo slow separation into portions that are readily redispersible in each other on mild agitation. The separation may be compared to the separation of cream or milk, the creaming being distinguished from sharpness of separation into distinctly defined layers.

Paraffin emulsion

A more specific example is the making of paraffin emulsion from the following ingredients.

	Parts
Monostearic acid amide of ethylene diamine	6
Stearic acid amide of hydroxyethyl amine (coupling agent)	12
Formic acid (85% solution)	1.25
Water	35.75
Paraffin wax	45
	100

The proportions may be varied from those given.

The acid used to solubilize the amine and thus produce the cationic material may be increased or decreased in amount, and may be replaced by acetic, hydrochloric, or like acid. Particularly desirable results are obtained when the proportion of cationic material to the coupling agent is about 1 to 2 and the ratio of the said material to paraffin wax is about 1 to 8. However, the cationic material may be used in proportions as low as 1 part to 25 parts of the wax and as high as 25 parts or more of cationic material to 25 parts of wax. The larger proportion of cationic material, however, is unnecessary and wasteful.

Oleic amides or other fatty acid amides may be substituted part for part for the stearic acid amide in the table.

The compound resulting from the treatment of the monostearic acid amide of ethylene diamine of the above formula with hydrochloric acid, for example, may be written as follows:



This compound serves as the cationic material, the chlorine becoming the negative ion when the compound is dissolved in water and the remaining complex organic part of the molecule becoming the positive ion.

The stearic acid amide of hydroxyethyl amine which serves as the coupling agent of the above formula may be written $C_{17}H_{35}CO.NH.C_2H_4OH$.

The following is a method that has been found satisfactory for preparing the paraffin emulsion: Melt the amide and coupling agent with the acid, at 70° to 80° C. Then add, as the dispersing medium, water which has been heated to 70° C. Stir until the whole is thoroughly emulsified. Melt the paraffin and add in small portions to the mixture made as above, with constant stirring. Keep the mixture at 65 to 70° C. (10° to 15° above the melting point of the wax) until all of the wax is admixed. Continue stirring the mixture until the temperature has dropped to 40° C. and the wax has, therefore, solidified.

This method results in a white, creamy emulsion paste which does not separate on standing.

Dilute emulsions are prepared by pouring water at 60 to 65° C. into the concentrated emulsion and stirring thoroughly, or by first pasting the

concentrated emulsion with a small amount of water at 60 to 65° C. and then adding the remainder of the water of dilution. The dilute emulsions are milky in appearance. When an electric current is passed through them, paraffin comes out on the cathode. This shows that the charge on the dispersed particles of paraffin is positive.

The method may be varied in many ways. Thus the emulsifier, coupling agent, and paraffin may be melted together and the acid and water then added. Or, the solid paraffin may be added to the emulsifier solution and the whole mixture heated and stirred until the paraffin is emulsified.

Carnauba wax emulsion

The emulsifier (basic compound adapted, to give the cationic material after neutralization), and the coupling agent are melted and the formic acid or other neutralizing acid is added, as at 70° to 80° C. A portion of water to be used is heated to 90° C. and added to the mixture, with thorough stirring. The carnauba wax is melted and added slowly and stirred into the mixture at 90° to 95°. After all of the wax has been thoroughly emulsified, the remainder of the water is heated to 95° C. and added slowly to the mixture. Care is taken to keep the temperature of the mixture between about 90° and 95° C.; at temperatures too low, the emulsion will not be satisfactory and above 95° C. or so the formic acid is volatilized at an appreciable rate. After all the water has been added, the mixture is constantly stirred until the temperature has dropped to 60° C.

The product sets, in time, into a stiff paste which is stable on standing.

Dilute emulsions of carnauba wax are best prepared by stirring the concentrated emulsion, prepared as above, in water at 90° to 95° C. The resultant dilute emulsions are opalescent and are not milky after cooling to 25° C. The carnauba wax is cationic, just as is the paraffin of the emulsion described above.

Various modifications in the details of the example may be made in the carnauba formula, as in the case of the paraffin emulsion, but about twice as large proportions of cationic material and coupling agent are required for best results with carnauba wax as with the paraffin wax.

The carnauba emulsions are useful in the treatment of leather.

Other materials that may be emulsified in manner described for carnauba and paraffin wax are waxes such as montan, spermaceti or beeswax.

Pigment dispersions

A typical pigment emulsion is made from the following materials:

	Parts
Monostearic acid amide of ethylene diamine.....	3
Stearic acid amide of hydroxyethyl amine.....	6
Water	9
Formic acid (85% solution).....	0.65
Titanium dioxide, finely ground.....	45
Water	36.35

The usual modifications can be made in this formula as to water content, ratio of cationic material and coupling agent to titanium dioxide, and other materials. Different acids also may be used.

The following procedure for preparation gives satisfactory results. Melt emulsifier (amide) and

coupling agent at 70° C. and add acid and part of the water. Paste up the titanium dioxide in the remainder of the water, at 25 to 30° C. Add the paste slowly, with constant stirring, to the emulsifier solution at 30° to 40° C.

The resultant product is a thick liquid or thin paste which is easily dispersed in cold water, to give a stable emulsion of the titanium dioxide. The titanium dioxide particles in the dispersion are cationic and are substantive for cotton, rayon and the like.

Other dispersible solids may be substituted for titanium oxide in the above example. Thus, there may be used zinc oxide, lithopone, ultramarine blue, or melted or powdered resins such as dammar, ester gum, or an alkyl.

Oil emulsion

An oil emulsion may be made from the following:

	Parts
Monooleic acid amide of ethylene diamine.....	6
Monooleic acid amide of hydroxyethyl amine.....	12
Formic acid (85% solution).....	1.25
Water	35.75
Mineral oil.....	45

The emulsion is prepared by the method described above the oil being stirred, say, at 50° to 60° C. or other elevated temperature.

Other oils may be substituted, as for example, castor, neat's-foot, and cottonseed oil.

Application of dispersions

The material or article to be treated with the dispersions made as described should be one which is substantive to the wax emulsion. The property of being substantive is not very well understood, but it may be due in important measure to a difference in the charge on the cationic compound and upon the material substantive thereto. Thus, the said material in contact with water may be electronegative or neutral, so that there is electrical attraction between the cation and the substantive material.

Among such substantive materials that may be used are cotton or rayon in the form of threads, yarns and fabrics, leather, wood, paper, and resinous compositions including nylon, vinyl resins, and the like. Cellulosic materials, particularly, are effectively treated with my dispersions.

Regardless of the particular dispersion chosen or the particular substantive material used, the product of the treatment gives thorough and satisfactory association of the dispersed particles with the substantive material. In case the dispersed particles are waterproofing or lubricating in nature, then these properties are imparted to the treated material, more or less in proportion to the amount of dispersion applied. When the dispersed particles are pigments, then pigmentation may be established; the principal advantage, however, in the use of dispersed pigments on textile threads or fabrics is flattening or dulling of the surface lustre. Thus, titanium oxide or zinc oxide pigment may be applied to rayon, to give a low-lustre rayon. When the dispersed material is resinous, then the treated article is modified as to surface hardness, resiliency, and impenetrability to water, the extent of the modification depending upon the particular resin chosen and the amount of it applied.

In general, treatment of penetrable materials with my dispersions gives not only a uniform

surface coating but also penetration somewhat beneath the surface portions of the material.

Special effects are obtained when a mixture of substantive and non-substantive materials is treated with my dispersions. There is partial taking, on the substantive material only. Thus, a fabric containing mixed rayon and silk, when treated as described, shows coating of the rayon, with a minor effect only or no effect on the silk. A pigment dispersion, say of titanium dioxide or zinc oxide, applied to a mixture of rayon and silk dulls the lustre of the rayon while leaving the silk substantially unaffected. Other mixtures that may be treated in this manner are those of silk or wool with paper, cotton, rayon or acetate silk.

Treatment of thread

A more specific illustration of the application of the dispersion is the treatment of cotton thread.

Thread in the form of skeins, packages, or warps is treated with a dilute bath of my cationic wax emulsions. The thread actually draws the wax away from the water and holds it. In this manner, even coatings of wax can be put on the yarn easily and cheaply.

As an example, I dissolve 1 pound of my concentrated paraffin wax emulsion in 100 gallons of water, at 90° F. I work 100 pounds of cotton thread in this bath, while raising the temperature of the bath to 140° F. As the yarn is worked in the bath, the milkiness gradually disappears; after about ten minutes, the bath is completely exhausted of paraffin.

The yarn is then extracted or squeezed and allowed to dry in an air dryer, at 100 to 110° F. After drying, the yarn has an even coating of paraffin and runs well in sewing machines.

Use of anionic material

When the material or article to be treated with my dispersion is not electronegative when in contact with water, then there may be used a pretreatment to make the material or article electronegative i. e. substantive to the dispersion. For this pretreatment, there is applied an anionic material such as a common soap, sulfonated castor oil, a wetting agent such as an alkali metal salt of a sulfate of a higher alcohol, or the like material that, when dissolved in water, gives an organic ion having a negative charge. Among such anionic materials that may be employed are sodium stearate, sodium dodecyl sulfate, and sodium salts of sulfonated higher alcohols.

The proportion of the anionic material used is ordinarily the minimum which will make electronegative the material or article to be treated with my dispersion. Ordinarily 1 percent or so of the anionic material is sufficient to make silk, wool, or like materials electronegative.

To the silk, wool, or other material so pretreated, my dispersion may be applied in the same manner as described above in connection with the treatment of cotton, cellulose, or thread.

It will be understood that the details given are for the purpose of illustration and that variations within the spirit of the invention are intended to be included within the scope of the appended claims.

I claim:

1. A dispersion including water as a liquid medium, finely divided water insoluble particles dispersed in the said medium, a surface active cationic compound, and a coupling agent, the cationic material being a water soluble organic compound that when dissolved in water gives a pos-

itively charged ion containing 6 to 20 carbon atoms, the coupling agent being an organic compound containing 6 to 20 carbon atoms to the molecule and selected from the group consisting of amides and higher aliphatic alcohols that is not ionized in water to a large extent and that contains a hydrophilic group, the coupling agent serving to stabilize the dispersion of the said particles in the medium, the said particles having a positive charge.

2. A dispersion as described in claim 1, the said water insoluble particles being normally electronegative and the cationic compound containing at least 6 carbon atoms in the part of the molecule that becomes the positive ion when the compound is dissolved in the medium.

3. A dispersion as described in claim 1, the cationic material containing an amino group in the part of the molecule that becomes the positive ion when the compound is dissolved in water and the coupling agent being substantially insoluble but dispersible in water.

4. A dispersion including finely divided water insoluble organic particles dispersed in a medium consisting largely of water, a dissolved organic compound giving in the aqueous medium a surface active organic cation, and a dispersed coupling agent, the coupling agent being a hydrophilic aliphatic alcohol containing at least 6 and not substantially more than 20 carbon atoms to the molecule and serving as a stabilizer for the dispersion.

5. A dispersion as described in claim 4, the coupling agent containing a hydroxyl and an amide group.

6. A dispersion as described in claim 1, the cationic compound including the salt of an acid with a higher fatty acid monoamide of an alkylene diamine and the coupling agent being a fatty acid amide of a hydroxyalkyl amine.

7. A dispersion as described in claim 1 including a pigment suspended in the said dispersion.

8. An aqueous dispersion for application to fibrous material that is electropositive when in contact with water, the dispersion including dispersed particles of wax, a fatty acid monoamide of an alkylene diamine, an acid neutralizing a portion at least of the amino group of the said monoamide of a diamine, and a fatty acid amide of a hydroxyalkyl amine, the particles including the wax being electropositive.

9. A dispersion as described in claim 1, the said dispersed particles being oil particles, and the cationic compound being the product of neutralizing with an acid a part at least of the amino group of a higher fatty acid monoamide of an amine, and the coupling agent being a fatty acid amide of a hydroxyalkyl amine.

10. A dispersion including finely divided water insoluble organic particles dispersed in a medium consisting largely of water, a dissolved organic compound giving in the aqueous medium a surface active organic cation, and a dispersed coupling agent, the coupling agent being a hydrophilic higher fatty acid amide containing 6 to 20 carbon atoms to the molecule and serving as a stabilizer for the dispersion.

11. A method of enhancing the surface modifying properties, in water-containing media, of cation-active surface modifying agents, which comprises admixing therewith an amide of an hydroxy-alkyl non-tertiary amine with a fatty acid containing 6 to 20 carbon atoms.

12. A treating bath containing water and having dispersed therein a cation-active nitrogenous

surface modifying agent and an amide of an hydroxy-alkyl non-tertiary amine with a fatty acid containing 6 to 20 carbon atoms, the amide being present in amounts less than the amount of the cation-active nitrogenous surface modifying agent.

13. A composition comprising a cation-active nitrogenous surface modifying agent and an amide of an hydroxyalkyl non-tertiary amine with a fatty acid containing 6 to 20 carbon atoms.

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