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WATER-THINNED PAINTS

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This invention relates to water emulsified protective coating compositions in general and more particularly to improved emulsifiers and emulsifier compositions for forming water emulsified coating compounds of various types such as paints, primers, varnishes, enamels, lacquer and the like material having improved film forming consistencies for brush, spray or other known means of application to surfaces of wood, metal, and the like materials and having superior finished protective coating characteristics particularly as to appearance and durability. This application is in part a continuation of a copending application by the present applicant and Glenn B. Weible as joint inventors, Serial No. 508,640, filed November 1, 1943, now matured into Patent No. 2,427,481.

It is well known that water emulsions have long been used for thinning protective coatings of various types. For example, the petroleum industry has emulsified asphalt to form a protective coating for roads, roofs, buildings, and the like uses. Similarly, inexpensive water-thinned paints have been sold for popular uses and these have, in general, been composed largely of casein containing various pigments. After evaporation of the water-thinner the casein is left as an adherent coating and cementing material which is thereafter practically insoluble in water but for outside use is subject to serious weathering and washing deterioration.

It is also well known to form paints, varnishes, and the like coating materials by emulsification of certain resins and oils together with water by various methods to form coating emulsions but the emulsions heretofore thus formed are known to have been unstable and the resultant dried coating formed by such water-paint mixtures have lacked the desirable characteristics of a conventional oil paint and insofar as is known, water has not heretofore been successfully used in connection with oleo-resinous coating compositions in such a manner as to preserve all of the desirable characteristics of the resultant coating usually associated with such oleo-resinous materials. For this reason water emulsified coating compositions have not heretofore been suitable for "outside" or similarly exposed surface application. Moreover, the emulsifying agents and compositions hereto known and employed have

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been highly selective in their effectiveness with respect to the type of coating compositions to which they were applicable, being entirely inoperative in many cases to produce stable emulsions with certain protective coating compositions.

In the beforementioned prior copending application, Serial No. 508,640, novel methods and materials were disclosed for rendering water-thinnable the conventional types of previously mixed, non-aqueous, unthinned concentrates of coating compounds such as the pigmented oleo-resinous paints and varnishes, enamels, lacquers, shellacs, and the like types of coating compounds which were intended by their manufacturers to be thinned with the usual non-aqueous water immiscible vehicles containing volatile and non-volatile, mineral and vegetable oils, or the like non-aqueous, organic solvents, diluents, dryers and carriers. Such so-called oil-thinned paints of the type are usually supplied to the consumer in the form of heavy pastes, or in any event in such concentrated form as to be non-fluid or highly viscous in consistency and they were, therefore, intended to be "thinned" or diluted prior to use with suitable quantities of thinners which heretofore have been the same or similar to those non-aqueous liquids initially present in small quantity in the concentrate vehicle. In such oil paints of the pigment filled type, the concentrates usually comprise solid pigments and fillers of the various metallic and mineral compounds ground in oil which may carry in solution both volatile and non-volatile constituents, certain gums and resins, and suitable dryers. Likewise, in varnishes, lacquers, and enamels which may or may not contain pigments, the vehicle may be a volatile solvent or a drying oil carrying a relatively large quantity of resin or resin forming material. The quantity of such "thinner" required or intended to be added to such paint, varnish and enamel concentrates to reduce them to liquid consistencies suitable for brush or spray application to surfaces to be coated, may range from approximately 30 to 80 percent by weight of the resulting thinned concentrate mixture as a whole.

As before stated, the beforementioned copending application disclosed novel and improved methods and materials for eliminating a substantial portion of the non-aqueous thinner here-

tofore required and instead rendering the pre-mixed non-aqueous coating composition concentrates thinnable with water to consistencies suitable for the various conventional means of application of protective coatings. The protective coatings resulting from that process had characteristics at least equal in quality to those formed by conventionally thinned oil types of paints and coating compositions and were superior to the usual water containing and emulsified types of coating compositions hereinbefore mentioned and heretofore employed.

The present invention is an improvement on the beforementioned water-thinned coating composition disclosed in copending application Serial No. 508,640 and is concerned with the formulation and original composition of the various coating composition emulsions from the several, separate, raw materials, of which they are usually comprised to form new, emulsified coating compositions which are in their ultimate applied condition not only similar in their desirable characteristics to the conventional, so-called oil-base types, but which are also superior to the emulsified and so-called water-thinned types heretofore known.

It has been found that substantially all of the known types of coating compositions such as paints, varnishes, enamels, lacquers, shellacs, and the like, can be compounded in emulsified form from their original constituents by the inclusion therein of the same emulsifiers as those disclosed in the beforementioned copending application, except it has been discovered that when the coating compositions are thus compounded from the several original constituents, it is no longer necessary to employ protective colloids to obtain stability. Thus it has been discovered that the employment of casein and other protective colloids can be entirely eliminated. This also appears to result in a dried, protective film which has greater imperviousness and density and higher gloss than the conventional water emulsifier paints heretofore known.

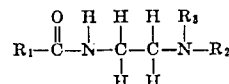
It is, therefore, an object of this invention to provide emulsified coating compositions which, for all practical purposes, manifest all of the desirable characteristics of the conventional or so-called oil-base or oleo-resinous types of paints and which, moreover, present spreading, film forming weathering and washing characteristics and appearance equal to any non-aqueous oil-base coating compositions, and superior in these respects to any of the emulsified coating compositions heretofore known. The objects of this invention are accomplished in general by emulsifying with water, substantially any of the usual types of natural or synthetic resins employed for coating materials, together with the desired pigments, plasticizers, driers, and relatively small quantities of solvents.

The emulsification of the several paint or coating composition ingredients with water is accomplished in accordance with this invention, in general, by milling one or a mixture of several of the usual types of natural or synthetic resins together with the desired fillers, pigments, and plasticizers, and a relative small quantity of non-aqueous solvent, in the presence of a dispersing medium or emulsifier comprising: water; an amido condensation product of the type formed by the reaction of a higher-fatty-acyl containing substance with an alkylene polyamine, or an alkylol amine, or an alkylol alkylene polyamine; and a supplemental emulsifying agent, such as

sulfonated castor oil, which is capable of exerting a supplementary emulsifying action. In some cases the presence of modicums of ammonia and/or Aerosol OT while not always necessary to the formation of the emulsion, facilitates the formation of the dispersion and enhances the spreading and leveling quality of the resultant coating composition.

Referring first to the beforementioned fatty-amido compound component of the dispersion medium, this compound may be any one of the types produced by the reaction of a fatty-acyl derivative containing from approximately 10 to approximately 22, and preferably from approximately 16 to approximately 22, carbon atoms with an alkylene polyamine, alkylol polyamine, or an alkylol alkylene polyamine.

In addition to the higher molecular weight fatty-acyl radicals, such amides may also contain amidified therewith other short chain acyl radicals such as acetyl radicals. An example of a preferred and superior substance coming within the latter class for employment in this invention is the fatty amide produced by reacting oleic acid and ethanol ethylene diamine, in the presence of acetic acid to form N-oleyl, N'-(acetyl-2-hydroxyethyl) ethylene diamine. The structure of this compound may be diagrammatically expressed approximately as:



where R_1 is an aliphatic high molecular weight portion of a fatty acid (alkyl derivative); R_2 is the -2-hydroxyethyl radical, and R_3 is the acetyl radical. Amides coming within the beforementioned class and requirement may be conveniently formed by reacting rice oil or soy bean oil and acetic acid with di-ethylene triamine or hydrogenated soy bean oil and acetic acid with ethanol ethylene diamine.

Higher molecular weight fatty acids which may be amidified as hereinbefore described are oleic, lauric, myristic, palmitic, stearic, hydroxy-stearic and palmitoleic acids and the like. The amide substitution portion may be derived from an alkylene polyamine, alkylolamine or alkylol alkylene polyamine, such as ethylene diamine, ethanolamine, diethylene triamine, ethanol ethylene diamine, tetra-ethylene pentamine, 1,3 diamine, isopropanol, and the like. The hereinbefore described condensation products will be, for convenience of description, herein referred to at times as fatty amides or amido compounds.

The supplementary oil-in-water emulsifying agents may comprise sulfonated fatty materials such as sulfonated castor, olive, sardine, peanut, and the like oils, sulfonated fatty acids such as sulfonated oleic acid and sulfonated fatty esters such as sulfonated isobutyl oleate.

As heretofore stated, substantially any of the original separate ingredients usually going into the formulation of the industrial non-aqueous water immiscible types of coating compositions and paints of the type for example common drying oil, pigmented paint, the oleo-resinous varnishes and enamels, the synthetic resin finishes and the cellulose esters, nitrates, acetates and ether lacquers and shellac coating materials, may be emulsified with water by employing the combination of the beforementioned dispersing medium in accordance with this invention. These coating compositions which may be so compounded may include small quantities of any of

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the usual thinners, solvents, fillers, pigments, plasticizers, resins, dryers, etc.

Referring now to the preparation or compounding of the water emulsified coating compositions employing the hereinbefore described emulsifier medium and coating compound ingredients, the preferred method is as follows:

The water in which the coating composition is to be emulsified, the fatty amido compound, and other emulsifying agents such as the sulfonated castor oil, are mixed in the proper proportion in any quantity desired. The thus pre-mixed water fatty amido compound and emulsifying agent may then be added with suitable stirring or agitation to the several previously mixed coating composition ingredients in the proper proportion and the resultant mixture preferably ground in a ball mill for approximately twenty-four hours.

The following basic formulation indicates in general an approximate composition of a pre-mixed emulsifying agent suitable for emulsifying the coating composition ingredients hereinbefore mentioned. The proportions given are approximate values and unless otherwise specified refer throughout the specification and claims to parts by weight:

	Parts
Fatty amide compound	24.7
Sulfonated castor oil	43.7
28% ammonia in water	20.4
25% Aerosol OT in water	11.2
	100.0

A number of water emulsified coating compositions which may be prepared applying the foregoing pre-mixed emulsifying medium are illustrated in the following examples, Nos. I, II, III and IV:

Example I

	Parts
"Pre-mixed" emulsifier	5.5
Nitro cellulose (refined)	11.1
Normal amyl methyl ketone	55.6
Water	27.8
	100.0

The mixture is stirred together and preferably ball milled for twenty-four hours. The resultant emulsified lacquer mixture has a fluidity and consistency suitable for application by the conventional spray gun painting equipment but may be further diluted with water if desired. The coating resulting from the application of this water emulsified lacquer upon surfaces such as aluminum alloy sheet metal panels by actual weathering tests and accelerated weatherometer tests results in protective and durability characteristics equal to those similar coatings formed in the conventional manner.

Example II

	Parts
"Pre-mixed" emulsifying medium	7.1
Rezyl 869	28.7
Zinc oxide	21.4
Butyl acetate	7.1
Water	35.7
	100.0

The mixture was milled together for approximately twenty-four hours and the resultant emulsion had a fluidity and consistency suitable for

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application to surfaces to be coated by spraying or brushing equipment. The resultant dried coating of the thus formed emulsion on metal has stability and durability characteristics equal to those formed by the conventional non-aqueous mixtures.

Example III

	Parts
"Pre-mixed" emulsifier	7.7
Cumar oleoresinous varnish	30.7
Zinc oxide pigment	23.1
Water	38.5
	100.0

The foregoing cumar oleoresinous varnish is of the type made by heating a drying oil, such as linseed oil, together with cumar resin in the presence of suitable driers and heating the mixture until the varnish has the required consistency, and may include a subsequently added diluent such as gasoline in an amount up to approximately 50%.

Example IV

	Parts
"Pre-mixed" emulsifier	7.7
Beetle 592-8	30.7
Antimony oxide	30.8
Butyl acetate	7.7
Water	23.1
	100.0

The Beetle 592-8 as employed in the foregoing formulation comprises an oil soluble urea formaldehyde resin procurable under that trade name from the American Cyanamide Corporation and includes approximately 50% of an aromatic solvent wet as xylene or toluene.

Numerous other types of water emulsified coating compositions may be formed in the foregoing manner, using approximately those proportions specified. Some variation in proportions, however, may be tolerated.

While the emulsifier mixture or "pre-mix" may be previously prepared in relatively large quantity for convenience in use and transportation and shipment and employed in the manner hereinbefore described, the separate ingredients of the emulsifier and coating composition constituents may, on the other hand, be mixed together without the formation of any pre-mixed portions thereof to form emulsified coating compositions of the types usually defined as the common drying oil-pigment paints, oleoresinous varnishes and enamels, synthetic resin finishes, the cellulose ester, nitrate, acetate and ether lacquers and the like, as follows:

Example V.—Urea formaldehyde type

	Parts
Fatty amido compound	2.9
Sulfonated castor oil	6.6
Beetle 277-8	29.5
Isoamyl alcohol	29.4
Ammonia (28%)	2.2
Water	29.4
	100.0

The Beetle 7542-10 and 277-8 are believed to be modified urea formaldehyde type resin obtainable under those trade names from the American Cyanamide Corporation and contain, as supplied, suitable quantities of plasticizers and diluents.

Example VI.—Silicone type

	Parts
Fatty amido compound.....	4.4
Sulfonated castor oil.....	6.6
Dow-Corning Silicone resin No. 990-A (60% solvent)	44.5
Water	44.5
	100.0

Silicone is the trade name for a polymerized silicon containing organic material obtainable from Dow Chemical Company.

Example VII.—Phenol formaldehyde type

	Parts
Fatty amido compound.....	3.0
Sulfonated castor oil.....	4.6
Bakelite 3962X.....	30.8
Xylene	30.8
Water	30.8
	100.0

Bakelite 3962X is a phenol or cresol formaldehyde type resin obtainable under that trade designation from the Bakelite Corporation.

Example VIII.—Melamine resin type

	Parts
Fatty amino compound.....	1.9
Sulfonated castor oil.....	.9
Melmac 246-10.....	18.4
Mono chlorobenzene.....	18.4
Antimony oxide.....	18.4
Ammonia (28%).....	.5
Water	41.5
	100.0

Melmac 246-10 is a Melamine-formaldehyde reaction product obtainable under that trade name from American Cyanamide Corporation.

Example IX.—Oleoresinous type

	Parts
Fatty amido compound	2.8
Sulfonated castor oil	4.2
Oleoresinous varnish and drier	28.2
Pigment	14.1
Gasoline	14.1
Ammonia (28%)	1.3
Water	35.3
	100.0

Example X.—Alkyd type resin

	Parts
Fatty amido compound	2.5
Sulfonated castor oil	3.7
Rezyl 869	24.9
Pigment (Titanox L)	12.4
Cobalt Nuodex	1.8
Lead Nuodex	1.8
Gasoline	18.7
Butyl acetate	3.1
Water	31.1
	100.0

Rezyl 869 is an alkyd type resin obtainable under that trade name from the American Cyanamide Corporation.

Example XI.—Vinylite resin type

	Parts
Fatty amido compound	2.9
Sulfonated castor oil	4.2
Vinylite VYHH	14.3
Xylol	28.7
Nitropropane	14.3
Isoamyl alcohol	7.1
Ammonia (28%)	7.1
Water	21.4
	100.0

Vinylite VYHH is obtainable under that trade name from Carbide and Carbon Chemicals Corporation.

Example XII.—Nitro cellulose lacquer type

	Parts
Fatty amide compound	2.3
Sulfonated castor oil	4.1
Nitro cellulose (½ sec. vis.)	10.7
Methyl normal amyl ketone	53.3
Ammonia (28%)	1.9
Aerosol OT (25%)	1.1
Water	26.6
	100.0

As stated in connection with Example II hereinbefore, the preferred method of forming the emulsified mixtures has been found to be to first stir the several ingredients of the formulation together and then to ball mill the mixture for approximately twenty-four hours.

In general, the amount of water specified in the foregoing formulation examples is satisfactory for brush application, however, in some cases it may be desirable to increase or decrease the portion of water to suit the different methods of application and surface and drying conditions. The exact permissible ranges of the proportions of the coating composition ingredients of the foregoing examples are not known, nor are the exact optimum proportions known; however, the examples give relative proportions which are known to be operative in the formulation of emulsified coating compositions which have excellent protective film forming characteristics.

In all cases the specified modicum of Aerosol OT may be omitted with some sacrifice in spreading and leveling characteristics. It will be noted that for some of the formulations no ammonia is necessary. However, in those formulations where ammonia is specified, it cannot be satisfactorily omitted.

Various water soluble supplemental emulsification agents in addition to the fatty amido compounds hereinbefore mentioned may possibly be employed but a 70% sulfonated castor oil, such as for example that obtainable from the National Oil Products Company, Inc., appears to be most satisfactory. The wetting agent Aerosol OT, which has been found desirable in some of the formulations, as indicated, is believed to comprise di-octyl sodium-sulpho-succinate and is obtainable from the American Cyanide Company. As before stated, Aerosol OT may be omitted, however, its presence is desirable to impart improved surface tension characteristics to the emulsion which will aid in the uniform spreading, leveling, and formation of an impervious covering for the various types of surfaces to which it is applied, particularly those which the emulsion would not otherwise readily wet.

While, in the foregoing description, typical ex-

amples of the more or less standard types of coating composition ingredients have been specified as being capable of being emulsified with water by means of the emulsifier of this invention, such specific ingredients do not appear essential to its broad application since, apparently, so far as is known, any type of the conventional coating composition ingredients as currently employed in the compounding of paints, varnishes, enamels, lacquers, shellacs and the like non-aqueous water immiscible coating compounds carrying natural or synthetic resins or plastics, or resin and/or plastic forming materials (oleo resinous materials) together with volatile and non-volatile solvents, drying oils, driers, plasticizers, and, if desired, carrying the usual paint pigments, may be emulsified with water in the manner of the present invention.

While preferred methods, materials and compositions have been described hereinbefore by way of illustrations, the invention is not to be limited thereby but is intended to cover any variation therefrom which falls within the spirit of the invention and the scope of the claims.

I claim:

1. An emulsified coating composition consisting essentially of from approximately 10 to approximately 45 parts of resin; approximately 2 to approximately 5 parts of an acetylated amido condensation product of a fatty acyl derivative containing from approximately 10 to approximately 22 carbon atoms, and a member of the group consisting of alkylene polyamines, alkylol alkylene polyamines, and alkylol amines; from approximately 1 to approximately 7 parts of a water soluble emulsifying agent, and from approximately 20 to approximately 50 parts of water.

2. An emulsified coating composition consisting essentially of from approximately 10 to approximately 45 parts of resin; approximately 2 to approximately 5 parts of an acetylated amido condensation product of a fatty acyl derivative containing from approximately 10 to approximately 22 carbon atoms, ethanol ethylene diamine and acetic acid; and from approximately 20 to approximately 50 parts of water.

3. An emulsified coating composition consisting essentially of from approximately 10 to approximately 45 parts of resin; approximately 2 to approximately 5 parts of an acetylated high molecular weight fatty amide of ethylene diamine containing from approximately 10 to approximately 22 carbon atoms; from approximately 1 to approximately 7 parts of a water soluble emulsifying agent, and from approximately 20 to approximately 50 parts of water.

4. An emulsified coating composition according to claim 1 in which the water soluble emulsifying agent comprises sulfonated fatty material.

5. An emulsified coating composition accord-

ing to claim 2 and further including a water soluble emulsifying agent comprising sulfonated fatty material.

6. An emulsified coating composition according to claim 3 in which the water soluble emulsifying agent comprises sulfonated fatty material.

7. An emulsified coating composition according to claim 1 in which the water soluble emulsifying agent comprises sulfonated castor oil.

8. An emulsified coating composition according to claim 2 and further including a water soluble emulsifying agent comprising sulfonated castor oil.

9. An emulsified coating composition according to claim 3 in which the water soluble emulsifying agent comprises sulfonated castor oil.

10. An emulsified coating composition consisting essentially of from approximately 10 to approximately 45 parts resin; from approximately 2 to approximately 5 parts of an acetylated high molecular weight fatty amide of ethanol ethylene diamine containing from approximately 10 to approximately 22 carbon atoms; from approximately 1 to approximately 7 parts sulfonated fatty material; from 0 to approximately 55 parts non-aqueous solvent; from 0 to approximately 7 parts ammonia (28%); from 0 to approximately 20 parts metallic compound pigment; and from approximately 20 to approximately 50 parts water.

11. An emulsified coating composition consisting essentially of from approximately 10 to approximately 45 parts of resin; approximately 2 to approximately 5 parts of an acetylated high molecular weight fatty amide of ethanol ethylene diamine containing from approximately 10 to approximately 22 carbon atoms; from approximately 1 to approximately 7 parts of sulfonated fatty material; from 0 to approximately 20 parts of a metallic compound pigment; from 0 to approximately 55 parts of non-aqueous solvent; from approximately 1/2 to approximately 20 parts of ammonia, and from approximately 20 to approximately 50 parts of water.

12. An emulsified coating composition according to claim 10 and containing a modicum of Aerosol OT.

ROBERT J. BURNS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,385,800	Douty	Oct. 2, 1945
2,384,081	DeGroote	Sept. 4, 1945
2,362,635	Howlett	Nov. 14, 1944
2,206,090	Haggenmacher	July 2, 1940
1,836,588	Gunther	Dec. 15, 1931