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TEXTILE COLORING EMULSIONS

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This invention relates to compositions useful for the coloring, printing, and decoration of textile materials, and is a continuation-in-part of my copending application Serial No. 52,599, filed October 2, 1948, now abandoned.

In the art of decorating and coloring textile materials there has been in use for a great number of years compositions containing soluble dyestuffs used both to effect over-all coloring and localized printing of designs on fabrics. More recently there have been proposed compositions in which the coloring material used is an insoluble pigment material rather than a soluble dyestuff. Compositions containing pigments rather than dyestuffs have several advantages, including resistance to fading, both from the effects of light and upon laundering, and when properly formulated can be used to print much more sharply and cleanly than can be done with dyestuff compositions.

The present invention provides compositions containing pigment coloring materials which can be used both for over-all coloring of textile materials and also for localized printing of particular designs, either upon an uncolored or a colored background on fabrics. These compositions of the present invention are emulsions in which water furnishes the continuous phase and in which a pigmented lacquer comprises one discontinuous phase.

In providing compositions in accordance with the present invention, it has been found to be completely satisfactory and economical to furnish a concentrate which subsequently can be diluted, if necessary or desirable, prior to use to furnish a material with the desired body for the particular operation by which such materials are applied to the fabric. In addition, the use of such concentrates enables the user to provide a material for printing which has the requisite shade necessary for the particular decorating operation, which may be accomplished by proper mixture of colors in a concentrate or by admixing in the proper proportions concentrates containing the colors necessary to give the shade desired for such operation.

By the present invention and as one aspect thereof, I have provided concentrates which are oil-in-water emulsions and which subsequently can be diluted, if desirable or necessary, by the addition of water alone, or by addition of water, mineral spirits and uncolored emulsions to provide finished compositions for application to fabrics.

In operations where a concentrate is furnished, the user may dilute such concentrate with wa-

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ter, hydrocarbon diluent and colorless emulsion until a composition of the necessary flow properties and containing the amount of coloring material necessary for a particular printing operation has been secured. Thereafter, if the coloring is to be effected by a printing operation, such printing is effected by utilization of the equipment ordinarily employed for such purposes. When printing is completed the colored fabric then is treated at elevated temperatures of the order of 300° F.-350° F. to effect removal of volatile material present and to complete the setting of the coloring material upon the fabric. Or, where padding or pad-dyeing is to be effected, the concentrates of the present invention may be diluted with water if necessary, or may be used without dilution to provide a composition useful for such purposes. Upon completion of the pad-dyeing operation, the treated material is likewise subjected to temperatures such as those suggested above to effect removal of volatile material and to complete the setting of the coloring material upon the fabric.

I have found that concentrates for such purposes must have a number of characteristics, all of which appear to be critical to secure a colored fabric, upon treatment as described above which has superior wash fastness, resistance to crocking, light fastness, hand, storage characteristics, handling characteristics, and padding properties.

There must be present in such concentrate a binder material which is present in an amount sufficient to bind the pigment coloring materials on to the textile fibers, enveloping and thus protecting the pigment particles and anchoring them on the exposed surfaces of the fiber. Since the padding or other operation by which the composition is applied to the fabric utilizes, according to the present invention, an oil-in-water emulsion, such binder material, since it is present in the discontinuous phase, is deposited as a discontinuous film. In addition to being present in quantities sufficient to bind the pigment material to the fibers, the binder materials should not be present in amount sufficient to objectionably affect the hand of the textile material. In other words, the amount of binder material should not be sufficiently great as to cause any objectionable stiffening of the colored fabric material. In accordance with the present invention I have found that the amount of binder material in such concentrate should not be present in an amount greater than 15 per cent of the concentrate, and as hereinafter described, must be made up of specific binder materials in order to secure the necessary satisfactory results.

In addition to the binder material in the discontinuous phase of the concentrate of the present invention there is present in this phase also the coloring material, which, according to the present invention, is an insoluble pigment. Further, in accordance with the present invention, there must be a critical ratio of total binder to pigment in order to secure satisfactory coloring of the fabric material and at the same time to insure adequate binding of the pigment to the fiber in discontinuous films, as above described. Utilizing the necessary quantity of resinous binder material above set forth, the ratio of total binder material to pigment must not be less than 15-12 and not more than 15-8.5 by weight to provide a product which has adequate coloring properties and which is firmly bound to the fiber.

In addition to the binder and pigment material the discontinuous phase of the concentrates of the present invention contains a mixture of materials which act both as a plasticizing mixture for the binder materials and as an emulsifier mixture to maintain the stability of the oil-in-water emulsion of the concentrate. I have found that the amount of such plasticizer-emulsifier mixture that must be employed in the concentrates of the present invention likewise is critical and must be sufficient to provide a concentrate which is stable upon storage and until the padding operation is completed and which, after the heating and curing imparts to the colored fabric sufficient flexibility without objectionably affecting the resistance of the colored material to fading or discoloration upon laundering. In accordance with the present invention particular plasticizer-emulsifier mixtures have been found to be necessary, as hereinafter described. When using such materials I have found that the necessary and critical amount can be determined by relationship to the amount of binder material employed. Using the quantities of binder as above set forth, the ratio of total binder material to the combined plasticizer-emulsifier mixture should be not less than 15-9.5 and not greater than 15-7.5 by weight.

The most satisfactory binder materials for utilization in concentrates of the present invention are mixtures of butylated melamine formaldehyde heat setting resinous condensates which comprise the reaction product of melamine, formaldehyde and butyl alcohol reacted to a point where the condensate is soluble in a mixture of equal parts of xylol and butanol, plus a cellulose ether material such as ethyl cellulose. In the concentrates of the present invention the amount of butylated melamine formaldehyde resinous concentrate utilized should not be less than approximately 11.2 per cent and not more than approximately 13.5 per cent by weight based upon the total concentrate. The amount of cellulose ether utilized should not be less than 1% and not more than 1.5% by weight based on the concentrate.

As pigment coloring materials there may be utilized either dry colors or press cakes or pigment pulps, where the latter are available. Also, in conjunction with and as part of the coloring material there may be employed fillers and extenders such as calcium carbonate, alumina hydrate, and the like.

The plasticizer-emulsifier mixture used in the concentrates of the present invention consists of a mixture of a thermoplastic alkyd resin, a non-ionic surface active agent, stearic acid and a

tertiary amine volatile at the temperatures reached during the curing or setting operation as above set forth. An alkyd resin which has a slight acidity is preferred, since such acidity will contribute to the emulsifying properties of the mixture. Non-ionic surface active agents such as polyether alcohols have been found, in accordance with the present invention, to be satisfactory for use as part of the plasticizer-emulsifier mixture. An example of such polyether alcohols is mono-iso-octyl-phenyl polyglycol ether, obtained by the condensation of ethylene oxide with monoisooctylphenol. The non-ionic properties and relative solubility in water and in oil make such materials useful for maintaining the stability of emulsion in both hard and soft water and in the presence of ions generally considered to be unfavorable to emulsion stability. In addition, the non-ionic properties of such surface active agent make such material effective under both the alkaline and acid conditions encountered in the manufacture and utilization of the concentrates of the present invention as hereinafter described. Stearic acid, combined with the tertiary amine forms a material which contributes to the emulsifying action and which imparts to the fabric after printing and curing a soft, smooth feel without causing any objectionable stiffening. The tertiary amine is necessary to form emulsifying soaps with the fatty acids present in the oil phase of the concentrate. Also, this material is employed to render the concentrate alkaline and sufficient quantity is employed to bring the pH of the concentrate and printing paste prepared therefrom to an alkaline condition. Under such conditions the concentrate does not gel or separate upon standing. Also, under such alkaline conditions there is no setting or separation caused by further polymerization of the butylated melamine formaldehyde condensate, since the latter materials do not further polymerize under alkaline conditions, but only under acid conditions. Because of the volatility of the tertiary amine at temperatures utilized in the setting and curing of the coloring composition, the amine is removed from the printed composition during such operation and thereby does not slow up or in any way affect the final setting of the printed composition which occurs upon curing at temperatures of the order of 300°-350° F. Materials such as diethylaminoethyl alcohol, triethyl amine, trimethylamine, stearyl dimethylamine and triethanolamine are illustrative of materials which satisfactorily may be employed.

In addition to the above materials there is present in the concentrates of the present invention a material such as phosphoric acid, salts of phosphoric acid or esters of phosphoric acid, in an amount not less than 0.15 per cent and not more than about 0.8 per cent of the concentrate. Such material is necessarily present in such amount to provide a satisfactory acid condition after removal of the tertiary amine during the curing operation to provide the requisite conditions for further setting of the melamine formaldehyde resinous material, which materials are thermosetting under such acid conditions at the curing temperatures above set forth.

The continuous aqueous phase of the concentrates of the present invention should be not less than about 40 per cent and not more than about 60 per cent of the total concentrate. The solids content of the concentrate must be not less than 25 per cent and not more than about

37 per cent of the concentrate. In addition to the materials above set forth, the remainder of the discontinuous phase of the concentrates of the present invention satisfactorily is made up of an aromatic hydrocarbon such as xylol. Such material promotes complete solubility with consequent intimate association of all of the oil phase soluble materials without softening or dissolving the pigment material. The film deposit, after curing, is thus homogeneous and is in intimate contact with the pigment material, which results in satisfactory effective binding of the pigment particles to the fibers.

Illustrative examples of concentrates of the present invention, showing compositions satisfactory for use in commercial operations are given below. In preparing such concentrates, satisfactorily all of the materials may be charged to a ball mill, and milled therein until the requisite dispersion and emulsification is completed. The material as discharged from the mill is ready for use.

Example I

Yellow Concentrate—Ingredients	Parts by Weight	Percent Solids
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 xylol-butanol).....	22.4	11.2
Xylol.....	3.4	1.0
Cellulose Ether.....	1.0	0.6
Alkyd Resin.....	0.6	0.5
Stearic Acid, double pressed.....	5.0	5.0
Non-ionic Surface Active Agent.....	2.0	0.2
Diethylaminoethyl Alcohol.....	0.2	6.9
Phosphoric Acid (85%).....	6.9	58.0
Benzidine Yellow Pigment.....	58.0	
Water.....		
Total.....	100.0	25.4

Example II

Blue Concentrate—Ingredients	Parts by Weight	Percent Solids
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 Xylol-Butanol).....	22.5	11.2
Xylol.....	4.2	1.3
Cellulose Ether.....	1.3	1.3
Alkyd Resin.....	0.8	0.8
Stearic Acid, double pressed.....	5.8	5.8
Non-Ionic Surface Active Agent.....	2.5	0.3
Diethylaminoethyl Alcohol.....	0.3	0.3
Phosphoric Acid (85%).....	44.4	10.0
Copper Phthalocyanine Blue Press Cake (22.6% solids).....	16.9	
Water.....		
Total.....	100.0	30.7

Example III

Gray Concentrate—Ingredients	Parts by Weight	Percent Solids
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 Xylol-Butanol).....	27.0	13.5
Xylol.....	5.0	1.5
Cellulose Ether.....	1.5	1.5
Alkyd Resin.....	1.0	1.0
Stearic Acid, double pressed.....	7.0	7.0
Non-ionic Surface Active Agent.....	3.0	0.4
Diethylaminoethyl Alcohol.....	0.4	11.4
Phosphoric Acid (85%).....	11.4	0.6
Carbon Black Pigment.....	2.65	
Copper phthalocyanine Blue Press Cake (22.6% solids).....	39.55	
Water.....		
Total.....	100.0	36.9

Example IV

Orange Concentrate—Ingredients	Parts by Weight	Percent Solids
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 Xylol-Butanol).....	27.0	13.5
Xylol.....	5.0	1.5
Cellulose Ether.....	1.5	1.5
Alkyd Resin.....	1.5	1.5
Stearic Acid, double pressed.....	1.0	1.0
Non-ionic Surface Active Agent.....	7.0	7.0
Diethylaminoethyl Alcohol.....	3.0	0.4
Phosphoric Acid (85%).....	0.4	12.0
Alkali Resistant Light Red Pigment.....	12.0	
Water.....	41.6	
Total.....	100.0	36.9

In the above illustrative examples, the cellulose ether employed was a low viscosity grade ethyl cellulose. The alkyd resin component of the concentrates was a non-drying oil-modified glyceryl-phthalate resin, and the non-ionic surface active agent utilized was mono-iso-octylphenyl polyglycol ether.

Another aspect of the present invention is the providing of compositions ready for use as oil-in-water emulsions for printing without further dilution with water, hydrocarbon materials, or colorless emulsions. Such compositions may be prepared either from the concentrates above set forth or directly from the starting materials, where desired. Such oil-in-water emulsion, in order to have satisfactory properties, as outlined above, must have a continuous aqueous phase containing not less than about 30 per cent and not more than about 35 per cent of water having dissolved therein a water-soluble thickening agent, a discontinuous phase of not less than about 55 per cent and not more than about 60 per cent of aliphatic hydrocarbon such as mineral spirits, and a discontinuous phase containing not less than about 2 per cent and not more than about 3 per cent by weight of butylated melamine formaldehyde resin condensate as above described, not less than about 0.25 per cent by weight of cellulose ether, together with pigments, the ratio of the combined melamine condensate plus cellulose ether to pigment being not less than about 15 to 9 and not more than about 15 to 6 by weight, aromatic hydrocarbon, not less than about .02 per cent and not more than about 0.12 per cent of a material such as phosphoric acid, a salt of phosphoric acid or an ester of phosphoric acid, and a plasticizer-emulsifier mixture, as hereinabove set out, comprising an alkyd resin, non-ionic surface active agent, stearic acid and a tertiary amine volatile at 300° F., where the ratio of the combined melamine condensate plus cellulose ether to the non-volatile combined plasticizer-emulsifier mixture is within the range of not less than 15-17 and not more than 15-12.5 by weight. In addition the emulsion to be satisfactory should have a pH within the range of approximately 8-10. For satisfactory operations the non-volatile content of the emulsion must not be less than about 6 and not more than about 10 per cent by weight within the limits as above set forth for the particular ingredients specified.

Such printing compositions may be prepared from the concentrates of the present invention. In so doing there may be used as a colorless oil-in-water emulsion satisfactory to effect dilution a composition such as the following.

Example V

Colorless Emulsion (Clear)—Ingredients	Parts by Weight	Percent Solids
Water	69.5	
Carboxymethyl Cellulose	10.0	10.0
Butylated Melamine Formaldehyde condensate (50% solids in 50/50 Xylol-Butanol)	10.0	5.0
Polyoxyethylene ether of sorbitan monolaurate	10.0	10.0
Diethylaminoethanol	0.5	
Total	100.0	25.0

With such colorless emulsion and concentrates of the present invention, compositions for effecting printing may be prepared. Examples of such compositions, illustrative of the present invention, are the following.

Example VI

Ingredients	Parts by Weight	Percent Solids
Clear of Example 5	10.0	2.5
Water	15.0	
Mineral Spirits	60.0	
Yellow Pad Dyeing Concentrate of Example I (25.4% Solids)	15.0	3.8
Total	100.0	6.3

Example VII

Ingredients	Parts by Weight	Percent Solids
Clear of Example 5	13.0	3.25
Water	17.0	
Mineral Spirits	58.0	
Blue Pad Dyeing Concentrate of Example 2 (30.7% Solids)	12.0	3.63
Total	100.0	6.93

Example VIII

Ingredients	Parts by Weight	Percent Solids
Clear of Example 5	15.0	3.75
Water	15.0	
Mineral Spirits	55.0	
Gray Pad Dyeing Concentrate of Example 3 (36.9% Solids)	15.0	5.54
Total	100.0	9.29

If, instead of preparing such compositions from the concentrates and colorless emulsions these materials are prepared directly from the starting materials, the proportions of materials used and illustrative satisfactory examples include the following.

Example IX

Ingredients	Parts by Weight	Percent Solids
Water	6.95	
Carboxymethyl Cellulose	1.0	1.0
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 xylol-butanol)	1.0	0.5
Polyoxyethylene ether of sorbitan monolaurate	1.0	1.0
Diethylaminoethanol	0.05	
Water	15.0	
Mineral Spirits	60.0	
Butylated Melamine Formaldehyde condensate (50% solids in 50/50 xylol-butanol)	3.36	1.68
Xylol	.51	
Ethyl Cellulose	.15	.15
Stearic Acid	.075	.075
Mono-iso-octyl-phenyl polyglycol ether	.75	.75
Diethylaminoethanol	.30	
Benzidine Yellow Pigment	1.035	1.035
Water	8.70	
Non-drying Oil-Modified glyceryl phthalate resin	.090	.090
Phosphoric Acid	.030	.026
Total	100.000	6.306

Example X

Ingredients	Parts by Weight	Percent Solids
Water	9.035	
Carboxymethyl Cellulose	1.3	1.3
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 xylol-butanol)	1.3	.65
Polyoxyethylene ether of sorbitan monolaurate	1.3	1.3
Diethylaminoethanol	.065	
Water	17.0	
Mineral Spirits	58.0	
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 xylol-butanol)	2.70	1.35
Xylol	.504	
Ethyl Cellulose	.156	.156
Non-drying oil-modified glyceryl phthalate resin	.156	.156
Stearic Acid	.096	.096
Mono-iso-octyl-phenyl Polyglycol Ether	.696	.696
Diethylaminoethanol	.30	
Phosphoric Acid	.036	.031
Copper Phthalocyanine Blue Press Cake (22.6% solids)	4.13 Water 1.2 Pigment	1.2
Water	2.026	
Total	100.000	6.935

Example XI

Ingredients	Parts by Weight	Percent Solids
Water	10.425	
Carboxymethyl Cellulose	1.5	1.5
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 xylol-butanol)	1.5	.75
Polyoxyethylene Ether of Sorbitan Monolaurate	1.5	1.5
Diethylaminoethanol	.075	
Water	15.0	
Mineral Spirits	55.0	
Butylated Melamine Formaldehyde Condensate (50% solids in 50/50 xylol-butanol)	4.05	2.025
Xylol	.75	
Ethyl Cellulose	.225	.225
Non-drying oil-Modified Glyceryl Phthalate Resin	.225	.225
Stearic Acid	.15	.15
Mono-iso-octyl-phenyl Polyglycol Ether	1.05	1.05
Diethylaminoethanol	.45	
Phosphoric Acid	.06	.051
Carbon Black Pigment	1.71	1.71
Water	5.93	
Copper Phthalocyanine Blue Press Cake (22.6% solids)	0.31 Water .09 Pigment	.09
Total	100.0	9.276

As described above, the concentrates referred to can be utilized as such and without any dilution for printing operations where desired. Also, the concentrates may be diluted with water to furnish a material satisfactory for pad dyeing operations or may be diluted with water, hydrocarbon diluent and colorless emulsion to provide a composition extremely satisfactory for utilization in printing operations.

While the above described products and processes of making the same constitute preferred embodiments of the invention, changes may be made therein within the scope of the invention as defined in the appended claims.

What is claimed is:

1. An emulsion comprising not less than approximately 40 per cent and not more than approximately 60 per cent by weight of a continuous aqueous phase, and a discontinuous non-aqueous phase, and containing not less than approximately 11.2 per cent and not more than approximately 13.5 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 1.0 per cent and not more than approximately 1.5 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus

ethyl cellulose to pigment being in the range of not less than 15 to 12 and not more than 15 to 8.5 by weight, aromatic hydrocarbon, not less than approximately 0.15 per cent and not more than approximately 0.8 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 9.5 and not more than 15 to 7.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 25 per cent and not more than approximately 37 per cent by weight.

2. An emulsion comprising not less than approximately 40 per cent and not more than approximately 60 per cent by weight of a continuous aqueous phase, and a discontinuous non-aqueous phase, and containing not less than approximately 11.2 per cent and not more than approximately 13.5 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 1.0 per cent and not more than approximately 1.5 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 12 and not more than 15 to 8.5 by weight, aromatic hydrocarbon, not less than approximately 0.15 per cent and not more than approximately 0.8 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and diethylamino ethyl alcohol, the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 9.5 and not more than 15 to 7.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 25 per cent and not more than approximately 37 per cent by weight.

3. An emulsion comprising not less than approximately 40 per cent and not more than approximately 60 per cent by weight of a continuous aqueous phase, and a discontinuous non-aqueous phase, and containing not less than approximately 11.2 per cent and not more than approximately 13.5 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 1.0 per cent and not more than approximately 1.5 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 12 and not more than 15 to 8.5 by weight, aromatic hydrocarbon, not less than approximately 0.15 per cent and not more than approximately 0.8 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, mono-iso-octyl-phenyl polyglycol ether, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 9.5 and not more than 15 to 7.5 by weight, said emulsion

having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 25 per cent and not more than approximately 37 per cent by weight.

4. An emulsion comprising not less than approximately 40 per cent and not more than approximately 60 per cent by weight of a continuous aqueous phase, and a discontinuous non-aqueous phase, and containing not less than approximately 11.2 per cent and not more than approximately 13.5 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 1.0 per cent and not more than approximately 1.5 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 12 and not more than 15 to 8.5 by weight, xylol, not less than approximately 0.15 per cent and not more than approximately 0.8 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 9.5 and not more than 15 to 7.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 25 per cent and not more than approximately 37 per cent by weight.

5. An emulsion comprising not less than approximately 30 per cent and not more than approximately 35 per cent by weight of a continuous aqueous phase having dissolved therein a water-soluble thickening agent, a discontinuous phase comprising not less than approximately 55 per cent and not more than approximately 60 per cent by weight of aliphatic hydrocarbon, and a second discontinuous non-aqueous phase, and containing not less than approximately 2.0 per cent and not more than approximately 3.0 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 0.15 per cent and not more than approximately 0.25 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 9.0 and not more than 15 to 6.0 by weight, aromatic hydrocarbon, not less than approximately 0.02 per cent and not more than approximately 0.12 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 17 and not more than 15 to 12.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 6 per cent and not more than approximately 10 per cent by weight.

6. An emulsion comprising not less than approximately 30 per cent and not more than approximately 35 per cent by weight of a continuous aqueous phase having dissolved therein a water-soluble thickening agent, a discontinuous

phase comprising not less than approximately 55 per cent and not more than approximately 60 per cent by weight of aliphatic hydrocarbon and a second discontinuous non-aqueous phase, and containing not less than approximately 2.0 per cent and not more than approximately 3.0 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 0.15 per cent and not more than approximately 0.25 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 9.0 and not more than 15 to 6.0 by weight, aromatic hydrocarbon, not less than approximately 0.02 per cent and not more than approximately 0.12 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and diethylamino ethyl alcohol, the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 17 and not more than 15 to 12.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 6 per cent and not more than approximately 10 per cent by weight.

7. An emulsion comprising not less than approximately 30 per cent and not more than approximately 35 per cent by weight of a continuous aqueous phase having dissolved therein a water-soluble thickening agent, a discontinuous phase comprising not less than approximately 55 per cent and not more than approximately 60 per cent by weight of aliphatic hydrocarbon, and a second discontinuous non-aqueous phase, and containing not less than approximately 2.0 per cent and not more than approximately 3.0 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 0.15 per cent and not more than approximately 0.25 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 9.0 and not more than 15 to 6.0 by weight, aromatic hydrocarbon, not less than approximately 0.02 per cent and not more than approximately 0.12 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, mono-iso-octyl-phenyl polyglycol ether, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 17 and not more than 15 to 12.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 6 per cent and not more than approximately 10 per cent by weight.

8. An emulsion comprising not less than approximately 30 per cent and not more than approximately 35 per cent by weight of a continuous aqueous phase having dissolved therein a water-

soluble thickening agent, a discontinuous phase comprising not less than approximately 55 per cent and not more than approximately 60 per cent by weight of aliphatic hydrocarbon, and a second discontinuous non-aqueous phase, and containing not less than approximately 2.0 per cent and not more than approximately 3.0 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 0.15 per cent and not more than approximately 0.25 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 9.0 and not more than 15 to 6.0 by weight, xylol, not less than approximately 0.02 per cent and not more than approximately 0.12 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 17 and not more than 15 to 12.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 6 per cent and not more than approximately 10 per cent by weight.

9. An emulsion comprising not less than approximately 30 per cent and not more than approximately 35 per cent by weight of a continuous aqueous phase having dissolved therein a water-soluble carboxymethyl cellulose, a discontinuous phase comprising not less than approximately 55 per cent and not more than approximately 60 per cent by weight of aliphatic hydrocarbon, and a second discontinuous non-aqueous phase, and containing not less than approximately 2.0 per cent and not more than approximately 3.0 per cent by weight of a butylated melamine formaldehyde resinous condensate, not less than approximately 0.15 per cent and not more than approximately 0.25 per cent by weight of ethyl cellulose, and pigment, the ratio of the combined melamine condensate plus ethyl cellulose to pigment being in the range of not less than 15 to 9.0 and not more than 15 to 6.0 by weight, aromatic hydrocarbon, not less than approximately 0.02 per cent and not more than approximately 0.12 per cent by weight of phosphoric acid, and a plasticizer-emulsifier mixture comprising a non-drying oil-modified glyceryl-phthalate resin, non-ionic surface active agent, stearic acid, and a tertiary amine volatile at 300° F., the ratio of the combined melamine condensate plus ethyl cellulose to the non-volatile combined plasticizer-emulsifier mixture being in the range of not less than 15 to 17 and not more than 15 to 12.5 by weight, said emulsion having a pH within the range of approximately 8 to 10 and having a solids content of not less than approximately 6 per cent and not more than approximately 10 per cent by weight.

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No references cited.