Patented Apr. 4, 1944 2,346,041

UNITED STATES PATENT OFFICE

2,346,041

PRINTING TEXTILES WITH PIGMENTS

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No Drawing. Application June 21, 1941, Serial No. 399,230

3 Claims. (Cl. 106—170)

This invention relates to the printing of textiles in colored patterns wherein the coloration is secured by pigments which are applied in and fastened to the cloth in a wash resistant manner by means of an emulsion of a new and novel composition.

The printing of textiles as normally practiced comprises essentially locally dyeing areas in order to secure desired designs. The dyestuff solution is applied to the cloth by passage of the cloth past an intaglio engraved roll, from which the cloth picks up the dyestuff solution. In order that sufficient quantity may be picked up and that it should not spread, it is essential that the dyestuff solution be thickened to a very heavy paste. This thickening is usually secured by the use of thick, heavy boiled starch pastes or by natural gum pastes, but the use of these materials interferes seriously with the securing of a high degree of sharpness. After the goods have been printed and dried, it is necessary that they be put through various steamings, aging operations, or other special treatments to cause the dyestuff to penetrate into the fibers or to chemically alter the nature of the dyestuff in order to secure the fixation on the cloth. This makes it very difficult and expensive to control shades and the printer never knows exactly what his work will look like until it has been put through a great many operations and subsequently washed, inasmuch as not all of the dyestuff is ever fixed to the cloth, and furthermore the thickener stiffens the cloth and must be removed from the fabric. Faulty printing and losses may occur at quite a number of steps and may reach serious proportions before it is discovered in later operations. Even after the goods have been washed in order to wash off starches and gums from the cloth, it is often found that these cannot be removed sufficiently and desizing operations are then applied in the case of cotton goods. In the case of printing on rayon, it is impossible to print with most of the commercial starches inasmuch as they cannot be removed from the rayon sufficiently and can only be removed by prolonged washing which with the light rayon fabrics is sufficient to distort the goods and cause severe damage.

In a copending application by one of the joint inventors of this case, Serial Number 386,627, filed April 3, 1941, it is shown that the use of soaps and suspended water-insoluble, solid fatty materials give pastes which are ideally suited for printing textiles in that they present a smooth, heavy body and after being printed on the fabric, they do not affect the handle and do not cause any stiffness where the goods are printed, thus it is possible to omit washing operations after printing in most cases.

We have found that pastes thickened by soaps and with suspended water-insoluble, solid fatty materials can be used to emulsify lacquers or solvents carrying binding resins or cellulose ester or ether compositions and that such compositions when pigmented are highly suitable for printing onto textiles and that color prints are thereby secured which show excellent fastness to washing and dry cleaning, a good resistance to rubbing, and a lack of stiffness or change in handle where the goods are printed. As most pigments are very fast to light, their use in this manner is attractive. The use of our emulsions offer a great many advantages to the printer. One of the most important advantages is that as soon as the goods are printed and come from the printed roll, the final shade and its completeness of coverage are immediately visible so that any defectiveness in work is immediately caught without any production of faulty goods.

Our printing pastes are printed from ordinary textile intaglio printing rolls. The use of our printing method is particularly attractive because of its simplicity, since as soon as the goods are printed and run over the dry cans, the cloth can be considered as finished, there being no necessity of further treatment to set the color such as occurs where dyes are used, and there is no necessity of washing out the goods such as is necessary where starches are used. The goods as they come off the dry cans are uniformly soft across the face, the paste having no stiffening effect whatsoever. This greatly simplifies printing and cheapens the cost of textile printing as well as diminishing serious rejections because difficulties are quickly caught in the first step of printing.

As our emulsions are dispersions of lacquer in a continuous water phase, it is very easy to clean this off of the machinery when it is desirable to change colors as the composition dilutes with water. Due to its high stability it does not coagulate or leave any stickiness on the printed roll, and it cleans out of the engraving quickly and completely. As our pastes dilute readily with water, it is possible to add at any time pigments dispersed in water. The use of our emulsion gives very sharp prints as the pigments, even when added in the form of water-dispersed pastes, appear to attach themselves to or to enter into the lacquer phase; and as the cloth is first wetted by the continuous or water phase, the colored oily lacquer shows no tendency whatsoever to spread

or run on the adjacent wet cloth. Our printing paste gives extreme sharpness which has never been secured by the use of starches or natural gums as printing vehicles. The pastes are very stable and may be kept for long periods and are not subject to bacterial attack as is true of the usual starches and gum thickeners. On the printing machine the extremely high stability permits the machines to run continuously without danger of the emulsions changing character or coagulating.

Pigmented emulsions employing water emulsified or dispersed in an exterior lacquer phase have been employed for printing textiles. Such emulsions have shown many difficulties in use. Where a lacquer is present as an exterior continuous phase, the printing paste is essentially the same as a lacquer in nature and is inflammable and whatever parts of the printing machines which come into contact with the solvents are immediately wet by the same, thus such emulsions when used in commercial printing machines have destructive action on the rubber blankets used in the machines since the solvents come in direct contact with the rubber and swell the same with rapid disintegration following. Likewise, this same type of lacquer emulsions irritate the human skin when they come into contact with the same. With water as the external phase in our emulsions we eliminate all of the above difficulties. Furthermore, if the attempt is made to add pigments dispersed in water, which is the normal way pigments are sold, to an emulsion having a continuous lacquer outer phase, the pigments will not mix in and the same is true if water is added since then water is essentially being added to an oily material. In consequence, the preparation of an emulsion printing paste with lacquer continuous phases involves complicated emulsifying machinery in order to beat in and atomize thoroughly the pigments and the water mixed in the ordinary dilutions, especially as it is desirable to add water for obvious economic reasons. Unless this job is done carefully, the emulsions show spottiness and incomplete coverage results when printed and where the dispersion is also not very good, the emulsion will soon break under the continuous agitating action of the printing roller dipping in the pan of color. In contrast, our new emulsion pigment printing media has a water exterior phase and, as such, water-dispersed pigment pastes may be added directly and merely stirred in without any special kind of apparatus. That our printing pastes are similar in many respects to a water paste is easily demonstrated by passing an electric current through our paste in series with an electric light. Our paste will conduct an electric current and light the light just as will a soap solution, whereas the pigmented emulsions which have, up to now, been employed in the textile printing art will not, as these have an oily outer continuous phase. As will be shown later, our pastes are extremely stable by reason of the very large amounts of stabilizer and dispersing agent used, and at no time is mechanical machinery necessary for the emulsification, the same being completely secured by hand if desired, giving globules of about one micron size.

The use of a lacquer dispersion in water as a printing paste is not normally possible due to the thinness generally found with such emulsions. It is only when the dispersed phase approaches 70–75% of the total liquid and is highly dispersed that the emulsion begins to show a high viscosity at all suitable for use as a printing paste. The use of such large amounts of lacquer, however, as an internal phase is obviously uneconomic as against printing where the lacquer is the external phase and need only be present to the extent of 25%. Thus, three times as much solvent would be necessary, and beside the added burden of cost the evaporation of such large volumes of solvent into the printing room atmosphere causes a very severe nuisance. In the securing of satisfactory sharp printing emulsions having a continuous water phase showing all the advantages of such emulsions, it was thus obviously economically necessary to find a means of securing thick pastes without the use of large internal dispersed lacquer phases.

It is an object of this invention to prepare printing emulsions having an exterior water phase useful as compositions for textile decoration which are inexpensive, involving a minimum of solvents, which emulsions are extremely stable.

It is a further object of this invention to provide a means of pigment printing on textiles which will give wash resistance and dry cleaning resistant prints.

We have found that by using high amounts of soap or soaps and suspended fatty materials in the water phase of our emulsions that we can secure oil in water emulsions which are suitable as cheap thickeners for printing and in which lacquer phases may be very simply emulsified, thus giving us cheap, stable emulsions suitable for printing of textiles with pigments. We have also found that the use of soaps in this manner does not hinder the deposition of the pigment on the cloth as the paste is dried out and does not affect the wash resistance of the deposited pigment adversely as one would expect from such powerful detergents as soaps. The wash resistance of prints made with our pigment pastes is very satisfactory. Furthermore, the use of soaps as a thickener does not give stiff deposits in the cloth, but rather leaves the cloth in a very soft and pleasing handle such that the printed portions feel as flexible as the unprinted portions. The printed cloth is highly water absorbent and in its soft printed condition can be used directly, and washing operations may be eliminated.

Thin printing inks for paper have been made which have used small amounts of soap as emulsifiers, but in insufficient quantity for the soaps to provide any thickness to the printing emulsion. Consequently, in both the paper and the textile printing arts, up to date, the emulsions used have been preferably of the water dispersed in oil type solely because in this type a minimum of solvent or lacquer phase could be used readily. Whenever the dispersed internal phase approached 75%, the globules then become so closely packed that they press closely one upon another and the separating films of the continuous phase become extremely thin. Under these conditions only do emulsions of two thin liquids show any desired thickness approaching a thick paste. With water as the internal phase this condition is easily secured under economic conditions, but to use 75% of lacquer as an internal phase is uneconomic. We secure stiff, and it is one of the objects of this invention to prepare stiff, thickened pastes, with lacquer as the internal phase where the percentage of lacquer or internal phase need not exceed 50% and may be as low as 20% or less. We are able to secure thick, heavy pastes which are oil in water emulsions with this relatively low internal phase volume of

lacquer or solvents by the use of an external phase which carries water soluble soaps in a relatively large percentage so that our external aqueous phase is of heavy viscosity. This water phase may carry in addition to soaps, suspended solid, insoluble fatty materials which further thicken the aqueous phase.

We prefer to use the water-soluble soaps of the fatty acids, such as, lauric acid, palmitic acid, stearic acid, and oleic acid with the alkalies, sodium, potassium, ammonium, borax or the organic bases such as ethylene diamine, triethanolamine and the other ethanolamines. The soaps are used in relatively large amounts, the amounts being present in the final printing paste being in excess of 3%. It is obvious that a much higher percentage of soap is actually present in the water phase. We find that an excess of fatty material is desirable over that combined with alkali for best stability and thickening value. We prefer to use in combination with our soaps, solid fatty substances, insoluble in water, such as, beeswax, Japan wax, solid fatty glycerides, glyceryl monostearate, and hydrogenated solid fatty esters; solid fatty acids, such as, stearic acid, palmitic acid, or mixtures of the same or solid hydrogenated fatty acids, and the solid glycol esters with the fatty acids, such as, diethylene glycol distearate, diethylene glycol monostearate, and propylene glycol monostearate.

The use of soaps as thickeners in printing pastes would be expected to be attended with the difficulty of foaming, and in some cases our emulsified lacquers show this tendency, but we have discovered that when our paste carries suspended fatty solid material that the latter act as anti-foaming agents. We may also add other anti-foaming agents such as, terpineols, pine oil, kerosene, naphtha, or octyl alcohol. The use of one or more of these materials is generally desirable and we add sufficient to our paste to prevent such troubles. In connection with the use of our fatty substances, we may use small quantities of anti-rancidity agents where desirable, such agents being those which are well known, and by preference we may use isothymol or the ethyl esters of parahydroxy benzoic acid.

From the standpoint of cheapness, we prefer to use as solvents in our lacquers those preferably of low cost; namely, ordinary hydrocarbon solvents. Some of these, such as, kerosene also have the advantage of preventing foaming. The choice of solvents to be used is also dependent upon the binders or lacquer resins to be used as these mostly have to be dissolved in the solvents. We have found terpineol or pine oil to frequently be very useful in this respect because of its cheapness and wide solvent powers as well as its anti-foaming properties. In general, we have found that solvents which are water soluble must be avoided where the binder is water insoluble since the use of such compositions results in immediate precipitation. Generally we find the addition of water-soluble solvents also has a thinning effect upon our emulsion paste. Preferably, then, we use solvents which are water insoluble and which are good solvents for the lacquer cellulosic bases or resin bases which are to be employed as binders for the pigments. Where mixtures of solvents are employed it is preferred that the active solvent should be of slightly higher boiling point than the diluents so that the last solvent to evaporate remains a good solvent for the lacquer. It is preferred that the solvents should have a boiling point above that of water so that after printing, the water is first removed by drying, leaving local deposits of the lacquer which thereafter proceed to dry to a uniform deposit with no precipitation difficulties. As would naturally be expected, the use of lacquer phases which are heavy and thick impart to the final printing pastes a somewhat higher viscosity, but it is impossible to secure a thick printing paste with 50% or less internal lacquer phase irrespective of its viscosity if insufficient soap is used in the water phase. That is, it is very important that the water phase must be very highly thickened.

As binders for fastening the pigments to the cloth, we may use materials soluble in either the solvent or the water phases. We may use lacquers composed of solvent solutions of ethyl cellulose, cellulose esters, such as, cellulose nitrate, cellulose acetate, or mixtures of these with resins and plasticizers. We may also use solvent solutions of alkyd resins, natural resins such as dammar, or the urea formaldehyde type resins or mixtures of these various resins with plasticizers where additional flexibility is necessary. We may also use the water-soluble urea formaldehyde resins dissolved in our aqueous phase in which case after printing and drying our cloth, we prefer that the cloth should be baked to further set the resin and make it thereafter water insoluble. Where we use a water-soluble, urea-formaldehyde resin, it is preferred that the soaps be used as thickeners should be ammonium soaps as the use of other soaps involving fixed alkalies interfere with the fixation of the resin.

Of the various binders we prefer to use ethyl cellulose as this material shows a maximum of flexibility and toughness. It is found that also where most other binders must be used to the extent of at least two parts for every one part of pigment solids employed, that only one part of ethyl cellulose is necessary to secure very good binding action sufficient to resist ordinary washing tests. We have found that ethyl cellulose prepared with an ethoxy content of 46.8 to 48.5% shows a maximum resistance to washing and we prefer the use of this material in any of the commercial viscosities available, but prefer to use the higher viscosity types such as the 100 viscosity. We may use the other types of ethyl cellulose of other degrees of ethylation, and we have found that the use of an ethyl cellulose of 43.5 to 44.5% ethoxy content, or even less, gives a maximum resistance to dry cleaning, and we may employ this type where the textile to be printed will be subject to such methods of cleaning. For general all around use showing a maximum resistance to both washing and dry cleaning, we prefer to use mixtures of these two types.

Printing pastes which are suitable for printing pigments onto textiles in accordance with our invention may be prepared in several ways. In each case we first dissolve the binding resin or cellulosic compound in the solvent for the same and in some cases we have found it possible to produce homogeneous solutions containing, in addition, at most, small quantities of water and the soaps dissolved along with the solvents and the lacquer ingredients. Such products containing our lacquer binder ingredients and our soaps for thickening means lend themselves to ready dilution with the formation of thick emulsion pastes when water is stirred into them.

Not all of the soap or thickening means need to be supplied in this way in a single product, but part of the soap may be dissolved in a separate

portion of solvent carrying no binder. This solvent solution containing either none or at most small amounts of water may then be diluted with larger volumes of water and give thick, stable emulsion pastes upon simple stirring. The pastes thus produced may be used as diluents or extenders for the pastes produced by the first method. It is perfectly obvious that the solvent solution of soap may also be blended with the lacquer soap solvent combination and thereafter diluted directly with water to form an emulsified paste. Perhaps one of the simplest ways of making our pastes is to merely dissolve the lacquer binding ingredients comprising the cellulosic compounds or resins in their active solvent and thereafter to add the diluting solvents while at the same time preparing an aqueous solution of soaps to the desired extent. The lacquer solution is then stirred into the thick soap suspension directly to again form an emulsion. In the fourth method, the fatty acids may be dissolved in the lacquer solvent solution and this may be stirred into an aqueous solution of alkali containing sufficient alkali to convert and form the desired amount of soaps. In any of these methods it is found that simple stirring suffices to produce a very stable emulsion, and in general it is found that in the thick pastes, the dispersed globules of solvent or lacquer phase are generally all around one micron in diameter. The methods of making our emulsions will be more specifically detailed in the examples which follow.

It is apparent that as our emulsions are oil-in-water type that water pastes of the ordinary textile thickeners such as starch pastes and natural gum pastes can be directly mixed with our emulsion thickeners which is impossible with emulsions of the water-in-oil type.

The pigments which may be used in our pastes as a means of printing may be insoluble metallic compounds such as titanium dioxide, zinc oxide, carbon black, yellow lead chromate, ultramarine, or they may be complex organic pigments such as the phthalocyanine compounds such as the Monastral blue and green pigments, or they may be other insoluble organic pigments such as the insoluble azo naphthol compounds such as para red or even insoluble oxidized vat color pigments. For use with our printing pastes, it is preferred that these pigments be ground and dispersed as water pastes as they are commonly supplied in the market for their various uses. Pigment pastes which are ground in oil can also be used, but these ordinarily must be emulsified into our pastes by the use of emulsification machinery. Oil dispersed pigment pastes can be added directly to our concentrated lacquer and soap base compositions before they are emulsified. Our preferred method of introducing the pigments is to add the water dispersed pigment paste directly to our printing paste emulsions after they have been slightly diluted with water so that they will stir in readily. Our emulsions may be used to print ordinary dyestuffs onto cloth in which case the dyestuff is merely dissolved in the water used in making the emulsion pastes.

It is found that when our pigmented printing pastes are examined under the microscope that in general the pigments are preferentially wet by the lacquer phases and are either found in the lacquers or at the interface.

It is found that the viscosity of our printing paste emulsions can be regulated to any desired thickness by merely adding further water to any given paste, or if additional thickness is desired, by adding more of the soap suspension or of the concentrated soap-lacquer base. The addition of small quntities of alcohols or other water-soluble solvents can be employed to reduce the viscosities when this is desired.

In the various compositions given in the following examples the parts indicated are parts by weight.

Example 1

A concentrated lacquer and soap base may be prepared by dissolving 5 parts by weight of 100 centipoise viscosity ethyl cellulose of 46.8 to 48.5% ethoxy content in 74 parts of pine oil and 12 parts of oleic acid. After securing a clear solution, a caustic soda solution comprising 1.6 parts of sodium hydroxide and 7.4 parts of water are stirred in. The excess oleic acid over that necessary for forming a soap aids in securing a clear, compatible solution mixture. The clear fluid solution may be shipped directly to textile printing mills and when desired for use by diluting with water there is formed the thick printing paste emulsion. In order to form the thick emulsion printing paste to 100 parts of this lacquer, we may add 95 parts of water with simple stirring. A paste is formed which increases in viscosity as more and more of the water is stirred in and shows a maximum body beyond which further addition of water causes a thinning. As the water is stirred in, there is produced a smooth, heavy, paste comprising an oil-in-water type emulsion. This paste is quite heavy and shows little tendency to flow. To the creamy paste we may then add, for example, 20 parts of Monastral Fast Blue BF pigment paste (E. I. du Pont de Nemours & Co., Inc.) which paste will contain approximately four parts of pigment solids. The pigment printing color is then ready for use and may be applied to the printing color boxes on the ordinary intaglio textile type printing machine, and it may be printed alongside of other types of colors and dyestuffs. Cloth such as 80 x 80 cotton cloth may be run through the printing machine and after drying on cans to remove the water and solvent the cloth is ready for use, if only our type pigment printing colors have been used thus avoiding the aging and washing treatment which are attendant upon the use of the ordinary dyestuffs printed with starch pastes. Designs printed in this way are very sharp and exceptional in their fine line reproduction. Prints secured with this paste were exceedingly good to washing. Printing runs with the emulsion showed no tendency to foam and long continuous runs of over 25,000 yards showed no tendency for the emulsion to break down or to coagulate. The stability of the emulsions were such that after three months' storage there were no changes in the thickness or in the particle size of the emulsions. The emulsion paste as printed contained 41.5% of dispersed interior lacquer phase. The paste also contained 5.9% soap and the exterior water phase contained all of the soap as a solution of 10.2% sodium oleate.

Example 2

To 43 parts of pine oil and 20 parts of the petroleum hydrocarbon distillate boiling between 310–390° F., boiling points (Varsol, Colonial Beacon Co.) we added 12 parts of oleic acid and 2.43 parts of 28% concentrated ammonia. A separate water solution was prepared which contained 70 parts of water and 12 parts

of a water-soluble urea-formaldehyde resin. This aqueous solution of binder was then stirred into the soap and solvent mixture and a thick oil-in-water type emulsion formed which was suitable as a printing paste. There was next stirred in 13 parts of Monastral Fast Blue BF pigment paste. The mixture was a stable, thick printing emulsion which was printed on cotton and dried on cans to remove the solvent and thereafter baked for three minutes at 300° F. to set the resin. The printed cloth was soft, sharply printed and resistant to dry cleaning and washing. The emulsion as applied to the printing machine had a solvent interior phase of 38% and an outer aqueous phase which contained 11.3% soap dissolved in the water or 6.9% ammonium oleate in the entire mixture.

Example 3

A concentrated lacquer and soap base may be prepared by adding to 70.5 parts of pine oil, 11.4 parts of oleic acid and five parts of diethylene glycol monostearate. In this mixture there are dissolved 4.75 parts of 100 centipoise ethyl cellulose of 46.8 to 48.5% ethoxy content. After the ethyl cellulose is dissolved, a caustic soda solution containing 1.25 parts of sodium hydroxide and 6.83 parts of water were then stirred in. The alkali is insufficient to convert all the oleic acid into soap. This gives a mixture which may be shipped to the textile printing mills and then diluted with water to form the printing emulsion. In order to form a printing paste emulsion there are added to 100 parts of this base mixture 120 parts of water which may be stirred in readily by hand or by paddles to form a smooth, heavy, creamy paste which is suitable for pigment printing. This paste would then contain 34.5% internal lacquer phase and a total of 5.56% sodium oleate soap. The aqueous phase would be a solution of 8½% sodium oleate soap and in addition to the dispersed lacquer phase there would be some dispersed water insoluble diethylene glycol monostearate present.

Example 4

A solution of 20 parts of pine oil and 13.3 parts of oleic acid was used to dissolve three parts of ethyl cellulose to form a clear lacquer solution. There is then stirred into this lacquer a caustic solution to form an emulsion paste directly, thus a caustic solution containing 1.9% parts of sodium hydroxide and 61.8 parts of water may be stirred into the lacquer and there is formed directly a dispersion of the lacquer in the water phase as a very heavy emulsion paste which is suitable for printing pigments. The paste thus formed contains only 23.1% internal dispersed lacquer phase. The mixture contains 15.3% sodium oleate which gives a concentration of 19.9% soap in the water phase.

Example 5

A concentrated lacquer and soap base suitable for shipment may be first prepared by mixing 43 parts of pine oil and 12 parts of oleic acid with 5 parts of 50 centipoise ethyl cellulose, 43.5 to 44.5% ethoxy content. After the ethyl cellulose has dissolved, 34 parts of a light hydrocarbon solvent of boiling point range from 315 to 387° F. (Gulf Solvent G-Gulf Oil Corp.) are added and a caustic solution containing 1.6 parts sodium hydroxide and 4.4 parts of water is then stirred in. The base up to this point contains 12.18% soap, 5% binder, 77% lacquer solvents, .70% oleic acid, 5.12% water. The slightly heavy solution produced may then be shipped to the point of use and when desired to make a printing paste, there is added to 100 parts of this base 70 parts of water and 10 parts of ethyl alcohol. This gives a smooth, heavy paste on simple stirring which is quite stable. In order to secure a yellow print there may be then added 30 parts of Hanza Yellow GDL pigment paste (15.75% solids) (General Dyestuff Co.). After stirring the pigment in well, the paste is ready for printing. This paste is somewhat thinner than would be the case of we used water in place of the ethyl alcohol. When printed onto cotton cloth and dried on ordinary textile steam cans to remove the solvents, the printed cloth was found to be very resistant to dry cleaning solvents and to washing. This paste as printed contained 41.7% internal lacquer phase. There was present in the mixture 6.1% sodium oleate soap which amounts to 10.4% soap in the water phase.

Example 6

In a mixture of solvents comprising 21 parts by weight of pine oil, 22 parts by weight of a petroleum hydrocarbon solvent high in aromatics of a boiling point range from 275–350° F. (Solvesso #2, Colonial Beacon Oil Co.) and 12 parts by weight of oleic acid, there was added 2½ parts by weight of 50 centipoise ethyl cellulose, 43.5–44.5% ethoxy content and 2½ by weight of 100 centipoise ethyl cellulose of 46.8 to 48.5% ethoxy content. After the ethyl cellulose has all been completely dissolved, 34 grams of the light petroleum hydrocarbon solvent used in Example 5 are then added and then a caustic soda solution containing 1.6 parts by weight of sodium hydroxide and 4.4 parts by weight of water are stirred in. This gives a concentrated lacquer and soap phase of a heavy fluid consistency which is a solution, and it may be shipped without difficulty. The base up to this point contains 12.18% soap, 5% binder, 77% lacquer solvents, .70% oleic acid, 5.12% water. When it is desired to make an emulsion suitable for printing from this base, there is added to 100 parts by weight of this base 150 parts by weight of water. To the thick creamy paste thus produced there are stirred in 20 parts by weight of Monastral Fast Blue BF pigment paste. This gives a printing paste which while thick enough for printing may be considered slightly thin by some printers, and in some cases a printer may desire the same to be thicker. The paste may be reduced in cost and increased in thickness by homogenizing into it 50 parts more by weight of the light petroleum solvent used in Example 5 (Gulf Solvent B). A smooth printing paste thus secured when printed from intaglio rolls onto cotton cloth gives prints which after drying on the cans to remove the solvents are very highly resistant to washing and dry cleaning. The final pigment paste formed in this example has an internal lacquer and solvent phase of 42.9%. There is present 4.0% sodium oleate in the entire mixture which contains 7.0% in the aqueous phase.

Example 7

A soap and lacquer emulsion base was first formed by preparing the following solution. After 11 parts by weight of stearic acid and 4.5 parts of 100 centipoise ethyl cellulose of 46.8% to 48.5% ethoxy content have been dissolved in 75 parts

by weight of pine oil an alkaline solution containing 2.11 parts by weight of monoethanolamine and 7.39 parts by weight of water are mixed in. This clear lacquer solution base may be shipped, and when it is desired to form a printing paste we take 100 parts of this base and stir into it 90 parts by weight of water. As we stir the water into our concentrated base, the same becomes white and progressively heavy as the water is stirred in, soon forming a very thick stable paste which is found to be an emulsion of the lacquer in the water. In order to make red prints we may add to the 190 parts of printing paste thus formed 30 parts by weight of Lithosol Fast Scarlet RF pigment paste, (13% solids, E. I. du Pont de Nemours). The red pigment paste is stirred in to form a smooth, uniform pigment color. In order to extend and cheapen the paste while still maintaining approximately the same printing viscosity, we may mix with this paste another emulsion printing paste which does not contain any binder. For example, we add 200 parts of a printing emulsion made by stirring together 5.52 parts by weight of oleic acid, 36.85 parts by weight of a light petroleum hydrocarbon solvent (Gulf Solvent B), 57 parts by weight of water and dissolved in the water 0.63 part by weight of sodium hydroxide. This latter emulsion will be found to be equally as heavy as the first one discussed above, and the two may be readily mixed in any proportion. In the proportions suggested the final printing paste would comprise of 38.2% internal dispersed lacquer and solvent phase and there would be present a total of 8.5% soaps in the water phase. In the entire mixture the soaps would amount to 5.2%, being 2.8% monoethanolamine stearate and 2.4% sodium oleate.

Example 8

A base product suitable for shipment to printing plants may be readily prepared in a semisolid form which presents advantages from the standpoint of shipments as contrasted to the liquid bases previously described. In this example, there is illustrated the use of a mixture of fatty acids, namely, stearic and oleic acid which may be deliberately mixed, or we may preferably use the commercial high titer red oil which is a mixture of stearic and oleic acid.

In 43 parts by weight of pine oil and 12 parts by weight of 28–30° titer red oil are dissolved by warming 2.5 parts by weight of 50 centipoise ethyl cellulose, 43.5 to 44.5% ethoxy content and 2½ parts by weight of 100 centipoise ethyl cellulose, 46.8 to 48.5 ethoxy content. This mix is thoroughly dissolved and 34 parts by weight of the light hydrocarbon mentioned previously as Gulf Solvent G is added while still warm. A caustic solution containing 4.4 parts by weight of water and 1.6 parts by weight of sodium hydroxide were stirred in to the above lacquer solution to form a heavy clear solution which on cooling sets up to a heavy, transparent, solid gel which can readily be cut into pieces. To form a printing paste emulsion 100 parts by weight of the above gel are mixed with 100 parts of water and stirred until heavy, smooth printing emulsions are secured. To obtain a green printing color 20 parts by weight of Monastral Fast Green GSF paste (21% solids, General Dyestuffs Corp.) are stirred in. The printing paste contains 5.82% sodium stearate and oleate soaps or 9.68% soap in the water phase. The internal lacquer phase was 39.9%.

Example 9

A concentrated lacquer and soap base was prepared by dissolving together 11.87 parts by weight of stearic acid, 4.86 parts ethyl cellulose, 81 parts of pine oil, and 2.27 parts of monoethanolamine. To 100 parts of this paste 90 to 130 parts of water were added. This gives a range of printing pastes of different viscosities, all of which are found suitable for printing with pigments after the pigment paste is added. If 90 parts of water are added the dispersed lacquer phase is 45.8%. If we use 130 parts of water, the lacquer phase becomes 37.9%. In a similar way the percent soap in the two pastes would be 9.9% and 5.6% and when calculated on the water phases present the monoethanolamine stearate soap would be 12.5 and 9.0% respectively.

The above descriptions and examples are intended to illustrate the nature of the invention, but the invention is not restricted to these examples.

We claim:

1. A self emulsifying base suitable for the formation of an oil in water emulsion textile printing paste by dilution with water comprising a binder selected from the group consisting of urea formaldehyde and ethyl cellulose 5%, lacquer solvents 77%, a water soluble soap of a fatty acid of at least twelve carbon atoms 12.18%, fatty acid of at least sixteen carbon atoms .70%, and water 5.12%.

2. A self emulsifying base suitable for the formation of an oil in water emulsion textile printing paste by dilution with water comprising ethyl cellulose 5%, pine oil and naphtha 77%, sodium oleate 12.18%, oleic acid .70%, and water 5.12%.

3. A self emulsifying base suitable for the formation of an oil in water emulsion textile printing paste by dilution with water comprising urea formaldehyde 5%, pine oil and naptha 77%, ammonium oleate 12.18%, oleic acid .70%, and water 5.12%.

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