United States Patent Office 3,086,873 Patented Apr. 23, 1963

3,086,873

SILK SCREEN PRINTING INK

Alexander H. Steinbrunner, 31 Anniston Drive, Dayton 15, Ohio

No Drawing. Filed Aug. 25, 1960, Ser. No. 51,779
24 Claims. (Cl. 106—24)

This invention relates to a novel ink-emulsion vehicle which is adapted for silk screen printing on a base to produce a decorative transfer sheet for heat release to an article to be decorated and to a transfer sheet embodying said ink.

The invention also relates to a novel method of manufacturing an ink-emulsion vehicle which is storage stable in a two-package system and which is capable of being formulated to adjust the silk screen printing results to variation in ambient relative humidity and temperature while providing excellent color reproduction, clarity and sharpness of definition in the color "half-tone" type of printing which is transferred from the transfer sheet.

The invention further relates to a method of decorating and printing by using an "iron-on" decal prepared with the ink-emulsion vehicle of the invention. The transfer sheet, which heat-releases an ink-resin color design to another object, after heat-ironing treatment is generally termed an "iron-on" decal.

"Iron-on" decals, like postage stamps, have the design imprinted on a releasable base of paper, cellophane, cellulose acetate, or sheet nitrocellulose and the design comprises a thermally adhesive ink-resin surface activated by heat applied to the back of the releasable sheet thereof to fasten it to the surface to be decorated by the transfer.

In the hands of the user, the transfer sheet is positioned in the preselected area over the fabric and heated with an iron to transfer the ink-resin dots in one or more colors. The face of the decal is frequently protected by a thin sized paper or fabric sheet which is removable when the decal is to be put in place.

The "iron-on" decals of the prior art have generally been made, heretofore, by printing with commercial printing machines, the design, usually in color, using special solid transfer ink containing wax and resin. The printing machine employed is provided with a "half-tone" printing surface. The design on the decal is thus the same as typographic printing from a "half-tone" plate and the decal serves to deposit the design in the form of a series of small colored dots of printing ink-resin vehicle from the transfer sheet to the object being decorated. These "half-tone" dots, therefore, take the form of a reverse pattern of the design on the decal so as to provide a positive image on the sheet or object which is to be decorated, usually a surface of metal, paper woven textile or other fabric.

The ink which is used to form the "half-tone" dots on the conventional "iron-on" decal is normally solid and becomes fluid when used with a heated letter press, litho and/or gravure printing machine. The printing machine is thus used to heat the ink to elevated temperature at which it is molten so as to provide a suitable printing consistency in making the decal. The print effect from the machine is obtained, therefore, by transferring a film of the ink in which there is no penetration to the fibers in an attempt to achieve the resultant clarity and sharpness of outline of the printed ink films after transfer from the decal. In contrast, the emulsion ink of the invention is applied not as a film from a "half-tone" printing plate but as a mass over the entire silk screen to the decal base and this mass nevertheless results in a series of separated color dot of solid ink, releasable by heat transfer to the object to be decorated.

In the conventional type of "iron-on" decal made by printing, the foundation material for the pigment or dye is usually made by combining several waxes and/or resins to design an ink which will soften in the temperature range used by the printing machine (generally 185–275° F). Waxes and resins of the ink vehicle although selected for specific qualities, must first meet the temperature requirements for transfer and of the printing machine and high melting waxes such as carnauba wax, beeswax and Montan wax are softened with lithographic varnish components, e.g., linseed oil or tung oil to provide proper working qualities of the ink and make it usable at high temperature on the "half-tone" plate. Heretofore, paraffin was was added to act as a release agent for the ink mixture (see Lawrence, U.S. Patent No. 1,939,821) and for this purpose was used in only minor proportion so that the wax base is essentially a high melting base rather than a low melting paraffin base. The essential solvent used for this high melting wax of the prior art is aromatic hydrocarbon. In contrast, the basic component of the wax of the invention is paraffin wax which softens in a lower temperature range than the waxes used in the prior art and which is effectively dissolved and dispersed in water medium by kerosene or similar aliphatic solvent. Further, the wax composition of the invention completely dispenses with synthetic or natural resins such as isobutylene polymer, gilsonite resins and phenolic resins which usually are added in the prior art to provide a proper balance of cohesion and adhesion and for desired viscosity at the melting range.

During heat transfer, the individually colored dots in the conventional "iron-on" decal tend to flow into each other, giving poor color definition, a muddy appearance and insufficient detail in the impressed design on the fabric. Thus, the results, despite the expense of manufacture of the decal, are considerably less than optimum for many decorative uses of these transfer sheets and considerable efforts have been made to improve the transfer ink.

In contrast, the present invention uses a specially formulated one-package or two-package aqueous wax emusion whose printing application is completely independent of the heating condition of the printing machine and which is applied in the cold by conventional silk screen application.

The present invention, thus makes possible the adaptation of the silk screen process for manufacture of transfers embodying multicolored ink dots. Surprisingly, the dots do not merge or run when applied as an emulsion in the cold. Heretofore, multicolored designs on painted tin cans and painted sheet metal advertising special signs made cheaply by the silk screen process have required special quick-drying paints which in turn require special resins, solvents, driers, and drying operations. These requirements are obviated in the aqueous quick-drying emulsion of the invention which omits special driers or unusual drying operations.

In conventional silk screening, a decorative design or lettering or other identification mark is applied to objects by means of the silk screens bearing the outlines of the design. The design is first made in a flexible metal, paper or similar backing by cementing a piece of silk or nylon. Nylon has replaced silk for most uses due to its higher tensile strength and durability. Paint or ink in bulk is forced through the meshes of the fabric by means of a stiff brush or a rubber squeegee after the screen is placed firmly on the object, or the paint may be sprayed through the screen.

The oil-in-water ink emulsion of the invention is specifically adapted for silk-screen printing because of the unique wax composition in the oil phase which provides a heat releasable and heat transferable wax film on the transfer sheet or on an iron-on decalcomania. The wax composition in the dispersed oil phase is a mixture of a low melting wax, an intermediate melting wax and a high melting wax, and the mixture melts in stages throughout the range from about 125° F. to about 210° F.

The low melting low melt viscosity wax is preferably petroleum or paraffin wax of melting range 125–165° F., the wider melting commercial waxes being preferred but mixtures of slack wax with ozocerite (50/50), with gilsonite (50/50) and with Utah wax (50/50) also being suitable, and is present in said mixture in a proportion of from 41–49% by weight of the total wax present.

The intermediate melting wax has a melting range of from about 142–150° F. Yellow beeswax, melting point 142–149° F., white beeswax, melting point 140–152° F. and Ghedda wax, melting point 141–151° F. are examples of suitable high melt viscosity waxes which are essential in the wax mixture to provide for high melt viscosity and high surface tension thereby facilitating silk-screen painting in the cold and transfer of the wax film under hot conditions.

The high melting wax has a melting range of between 180–187° F. The high melting wax imparts hardness and includes carnauba wax, melting point 180–187° F., Montan wax, melting point 165–170° F., Ouricuri, melting point 180–187° F., these waxes alone or in admixture with each other.

A liquid vegetable oil plasticizer is present with the wax mixture being in an amount of from about 24–30% of the total weight of said wax and oil.

A hydrocarbon solvent for said wax mixture is used, said solvent having a boiling point of from 100–250° F. constituting from about 44% to 52% of said oil phase, and serving as the volatile carrier for said wax and vegetable oil plasticizer.

A stabilizing agent is essential in the water phase, this agent including as the essential ingredient milk protein in an amount of from 2–8% of said water phase which is dispersed by an amount of about 0.1 to 0.4% of soap and 0.05 to 0.2% of borax to interact with said milk protein as the sole alkaline agents in said water phase.

Thus, in contrast to the convention oil-in-water pigment emulsion which is specifically formulated to deposit a continuous film of the binder by virtue of adding surface tension reducing emulsifying agents, the emulsion wax vehicle of the present invention is formulated for an opposite purpose to prevent forming a continuous film. The alkali metal soap and/or an alkali metal borate interact with the milk protein to provide only limited surface tension reduction. Since these constitute the only alkaline materials for aiding dispersion of the milk protein in the water phase, the alkaline emulsifying complex effectively limits the film flow of the dispersed wax particle during silk screen printing. There is retained in the oil phase a wax component having substantially high viscosity and high surface tension. The deposit of discrete color dots of film by forcing the emulsion in bulk through the openings of the silk screen remains fixed in place in the transfer sheet. The high surface tension of the liquid dots helps retain the spacing on transfer. Also the alkali metal borate treated milk protein does not appear to significantly alter the wax melt viscosity at the high temperature used in heat-transfer. The protein is effective to prevent coalescence of the deposited wax dots into a continuous film in the presence of the organic solvent which is also present in the oil phase.

The water-immiscible organic liquid solvent has a boiling range of from 100–250° F. and is a good solvent for the wax binder and vegetable oil plasticizer. Although the choice of solvent may depend to some extent upon the pigment or dye which is employed, it is preferred to combine an aromatic or naphthenic high solvent power solvent with a paraffin solvent, such solvents as benzene, toluene or xylene are blended with solvent naphtha, kerosene, and white spirit. It is necessary that the amount of solvent employed vary between rather narrow limits when substantial amounts of cheaper low solvent power paraffin solvents are used, e.g., between about 44 to about 52% of the oil phase. If too little solvent is present, e.g., from about 25–35% of the mixture of 15–25% aromatic hydrocarbon solvents and 85–75% of paraffin solvents with the wax present in an amount of more than 65%, then the wax emulsion is too heavy, very difficult to form and too thick to use in the silk screen process. If the amount of solvent is too much, e.g., about 60%, the solvent mixture acts to promote continuous film formation and there is not achieved the desired deposit of separate discrete and sharply defined color dots by cold application through the silk screen.

If minor amounts of stronger volatile solvents are added, such as petroleum ether, carbon tetrachloride, etc., the amount of aromatic or naphthene solvent should be reduced. Cheaper types of naphthene and paraffin solvents are preferred since they require less skill in handling and produce, in most cases, more uniform and better silk screen printing results.

All of the solvents used are volatile at room or moderately elevated temperature and may be termed "evaporative" water immiscible organic liquids. In general, any combination of petroleum distillate of paraffin structure and coal-tar distillate of naphthene or aromatic structure having a wide boiling range in the range of about 100° F. to 250° F. will provide desirable silk screen printing results.

The essential emulsifying ingredient of the invention, the alkaline soluble milk protein, is preferably used in the form of evaporated or condensed milk. The protein in condensed milk may amount to not more than 25% of its condensed solids, e.g., 100 grams of condensed milk may contain about 8 grams solids of which about 2 grams are the essential protein constituent, however, there may be up to four times this amount of protein employed. In milk the protein is acidic and is believed to react in the same manner as dry milk protein and casein with the alkaline borax and soap to form a more soluble protein, possibly caseinate in the presence of milk fat which is soluble in the water phase. The milk protein is rendered more soluble in the aqueous phase of the emulsions by means of alkaline soap, e.g., sodium oleate, potassium oleate, sodium stearate, potassium stearate, and borax. Thus, the emulsion composition may be diluted more readily with solvent, e.g., kerosene or with water to the extent as may be required for various uses.

Other water-soluble proteins than milk protein, for example, gelatin, water-soluble albumins, alkali-soluble, acid-precipitable casein and soy bean protein may be included with milk protein as desirable ingredients in the wax phase of the emulsion but the protein stabilizer must include milk protein as an essential ingredient.

When the ink is to be used, emulsifying agents may be added if desired by the printer under circumstances where a very thin coating is wanted. Such emulsifying agents are not necessary but when added it is preferred to include acid, sulfuric acid esters of fatty alcohols, sulfonated castor oil, higher alkyl sulfonates, higher hydroxyalkyl sulfonates, sodium α-hydroxyoctadecane sulfonate, sulfodicarboxylic acid ester, for example, the sodium salt of sulfo-succinic acid dioctyl ester, higher alkyl-aryl sulfonates, and polyglycol ethers of fatty alcohols of higher molecular weight, such as cetyl, oleyl or octadecyl alcohol, for example, reaction products of 15–30 molecular proportions of ethylene oxide with 1 molecular proportion of a fatty alcohol. There may also be used emulsifying agents having a pronounced wetting action, such as octylphenol polyglycol ether, acid sulfuric acid esters thereof, and also dodecyl alcohol polyglycol ethers.

Particularly, emulsifying agents in these cases are:

1,6-dilauryl diglycerol
Mono-abietic acid ester of triglycerol
Mono-stearyl glycerol
Mono-cetyl ether of glycerol
Mono-oleyl glycerol
Di ethylene glycol mono-stearate

With respect to the pigments or fillers employed, if a white ink is desired, lithopone, zinc oxide, titanium oxide and barium sulfate or other white pigments as desired. Venetian red, is a suitable pigment for use if a red coating is desired.

Lake pigments, such as those of the alizarine lake type, and those formed by the combination of a basic dye with a hetero-polyacid containing a plurality of radicals of phosphorus, tungsten, molybdenum, and silicon may be used especially those which are formed by the combination of a basic dye with a phosphometal acid (phosphotungstic acids, phosphomolybdic acids, phosphotungstomolybdic acids). Also dyestuff materials such as organic pigments anthraquinone dyes and insoluble azo compounds may be used such as

Kiton Blue A (Colour Index Supplement, page 44)
Orange II (Colour Index Supplement No. 151)
Alizarin Sapphire Blue B (Colour Index No. 1054)
Benzyl Green B (Colour Index No. 667)
Orange R (Colour Index No. 161)
Brilliant Kiton Red B (Colour Index No. 748)
Acid Violet 6B (Colour Index No. 698)
Acid Green (Colour Index No. 660)
Direct Fast Orange SE (Colour Index No. 326)
Cotton Fast Blue 3G (Colour Index No. 503)
Carbide Black ER (Colour Index No. 582)
Thioflavin T (Colour Index No. 815)
Rhodamine B (Colour Index No. 749)
Cotton Yellow CH (Colour Index No. 365)
Chlorantine Fast Red 7B (Colour Index No. 278)

Following is a summary of the composition features of the emulsion ink of the invention adapted to be used with the dyestuffs and pigments indicated:

A. FILM BINDER COMPOSITION PROPORTIONS

1. WAX AND PLASTICIZER PROPORTIONS IN THE OIL PHASE

Wax or Plasticizer component	Range, Percent	Preferred, Percent
Paraffin	30-36	33
Beeswax	18-22	20
Carnauba wax	18-22	20
Linseed oil	24-30	27

2. OIL PHASE PROPORTIONS, WAX AND HYDROCARBON SOLVENT

Total wax composition	48-56	52
Total solvent composition	52-44	48

3. WATER AND OIL PHASE PROPORTIONS

Total wax and linseed oil plasticizers	17-27	20-25
Total solvent	16-22	18-20
Stabilizing agents, milk, soap and borax (dry weight)	10-16	12-14
Total water	57-35	50-41

4. STABILIZER IN THE WATER PHASE

Ingredients:		
Percent soap (dry basis)	.1-.4	.2
Percent borax	.05-.2	.1
Percent water	91-93	92
Percent milk solids (butter fat) (casium, etc.)	9-6	8

The present invention is believed to be the first to provide means enabling a commercially practical cold silk screen process for effecting transfer sheets for "iron-on" decals by providing a novel ink emulsion base uniquely enabling the economical printing of "iron-on" decals and the entire elimination of the heated printing equipment which was used heretofore. Moreover, the invention provides an improved means for cold application of predetermined color dots to a transfer sheet in precisely defined relation with water soluble or water insoluble colors and in an aqueous medium so the colors can be transferred therefrom with complete definition, clarity and uniformity as to detail. The "iron-on" decal thus provided enables a better and more lasting image reproduction on fabric than was previously possible.

The following examples, in which all of the formulae are given in parts by weight of the several materials, will serve to illustrate the invention:

Example 1

An emulsion ink vehicle in accordance with the invention which is specifically adapted for silk screen printing to manufacture iron-on decals is formed of three significant mixtures in a two-package system including a thinner composition and two vehicle or base compositions. The thinner and base compositions are combined in limited proportions to provide an emulsified product to suit the climate to which the ink is to be subjected.

A preferred thinner "A" has the following composition by weight:

	Percent
Xylol	30
Naphtha	60
Kerosene	10

The first base mixture "B" has the following composition by weight:

	Percent
Paraffin wax	8
Beeswax	5½
Carnauba wax	9
Kerosene	10
Linseed oil	5
Thinner "A"	7½
Soap (soft)	10
Milk (condensed)	44
Borax	1

The second base mixture "C" has the following composition by weight:

	Percent
Soap (soft)	7
Milk (condensed)	55½
Linseed oil	7
Beeswax	3½
Paraffin wax	7
Kerosene	20

In forming the ink base, the thinner "A" is first mixed at room temperature. The three ingredients, xylol, naphtha and kerosene, are weighted, placed in a glass container, or its equivalent and shaken well to effect a mixture at normal room temperature conditions.

The base mixture "B" may be prepared as follows. The proper percentages by weight of the three wax ingredients are placed in a metal or equivalent container and melted together at approximately 200° F. and allowed to cool to about 150° F. The indicated proportion of the thinner "A" is then added and stirred in to provide a mixture having a light "cream" consistency. Then the kerosene and linseed oil are stirred in, the whole mixture being effected at a temperature of approximately 150° F. The blending of the melted waxes and the thinner "A" first eliminates the possibility of formation of lumps of wax which will not pass through woven silk and insures an extremely smooth "cream" consistency of the mixture. The mixture is then allowed to cool. If desired, at this point a small amount, up to ½% by weight, of a wetting agent, glycol mono-oleate may be added to increase the working freedom of the waxes.

However, this is not essential to the making or usage of the composition. In the event the wetting agent is added, the resultant mixture must be left to stand for at least 24 hours to permit the wetting agent to conventionally function.

The soap and borax of the composition "B" are separately mixed at room temperature and the condensed milk stirred in to provide a product having a soft "cream" consistency. The soap, milk and borax thus mixed are then added to the previously mixed waxes, thinner "A," kerosene, and linseed oil and the whole is blended to a fine "cream" consistency by beating or stirring it vigorously with a paddle or an equivalent device. This produces a completely stable emulsified product "B" which may be stored almost indefinitely in any climate.

The mixture "C" is formed by first melting the beeswax and paraffin wax together at a temperature in the neighborhood of 200° F. To the melted waxes is added a mixture of linseed oil and kerosene in the amounts given above. The condensed milk and soap mixture are then added with efficient stirring to the mixture of beeswax, paraffin wax, linseed oil and kerosene. After efficient mixing the mixture "C" is brought to a light "cream" consistency by continued stirring at room temperature. The emulsified product "C" is completely stable in storage for an extremely long time, e.g. 6 months or longer under the normally encountered storage conditions.

Each of the base compositions "B" and "C" are combined to provide an ink base for pigmenting which is useful for an effective silk screen printing process for producing transfer sheets and iron-on decals. A preferred combination of the base "B" and "C" for this purpose consists of 60% "B" and 40% "C" by weight, these proportions varying from 40–75% of B and 60–25% of C. By mixing in suitable blending equipment, an ink base is provided which will serve as a vehicle for wash out ink (water soluble ink) or permanent type dye. Depending on the climate where the ink base is to be employed, the composition of the ink base may range from 40% to 75% of the base "B" by weight.

The product resulting is thoroughly emulsified and on mixing of a dye therein provides an ink which will readily flow through silk at ordinary room temperatures. This ink also has the characteristic of hardening on exposure to air at ordinary room temperature.

Example II

In this example pigmented types of aqueous emulsion ink compositions are described.

The base mixture "B" and the base mixture "C" of Example I are mixed in 50/50 proportions by volume. Venetian red pigment in an amount of 42% by weight of combined "B" and "C" is carefully blended in by stirring with efficient mechanical stirring at room temperature for 3–4 hours. The red colored emulsion is applied by silk screen to form red colored dots on a cellulose acetate film base to make an iron-on decal. A flat iron, electrically heated to 200–225° F. serves to transfer the red dots of the image to a paper sheet.

Example III

This example illustrates variations in the wax composition.

In similar manner to the preparation of Example I, thinner "A," first base mixture "B," and second base mixture "C" are mixed. The only change which is made in the formulation is to substitute in mixture "B" and in mixture "C," a mixture of slack wax and ozocerite, there being present 50 parts of each of these waxes in the petroleum wax component. This petroleum wax mixture melted in the range of 120–160° F. Ozocerite was added in the proportion varying from 30–70 to 70–30 to the slack wax. Upon combining the so modified mixtures "B" and "C" as set out in Example I, an ink pigment as in Example II produced satisfactory iron-on decals on cellulose acetate.

Similarly the petroleum wax of Example I was changed to a mixture of slack wax and gilsonite, a further embodiment was a mixture of Utah wax and slack wax. In both of these latter compositions the gilsonite and Utah wax were used in varying proportions with slack wax from 70–30 to 30–70 by weight. Similar satisfactory decals were produced.

A further formula was made in which the high melting wax component, carnauba wax of base "B" in Example I was substituted in the same amount with Montan wax. Equally good results were obtained in the final decal printed by the silk screen method.

A further formula was prepared utilizing Ouricuri wax instead of carnauba wax in Example I.

Still another mixture was made in which the petroleum wax component in each of formulas "B" and "C" is a mixture of equal parts of slack wax, Japan wax and gilsonite.

Each of these latter formulations provided excellent iron-on decals.

Example IV

This example illustrates variation of the oil plasticizing component. The method for formulation is the same as in Example I, the method of pigmentation and application of the ink by silk screen printing is as set out in Example II. The variation illustrated in this example is by substituting in the same proportion as set out in Example I, tung oil, castor oil, and a 50/50 mixture of wool fat and linseed oil.

Each of the foregoing formulations provided satisfactory iron-on decals in accordance with the procedure in Example II.

In the foregoing examples there are illustrated various wax emulsion ink formulations based upon kerosene as the essential solvent, milk protein as the essential stabilizing agent and a vegetable oil as the non-volatile wax plasticizer for a petroleum based wax. The petroleum wax based composition exhibits a melting range in the temperature interval for decal transfer by a hot iron, e.g. from 125 to 210° F. In each instance of printing the discrete separate dots were formed on the decal and transferred from the decal to a receiving sheet in unimpaired condition without loss of clarity, spacing or dimensions.

In each case the printing on the transfer base sheet, nitrocellulose, cellulose acetate, Holland cloth, at room temperature resulted in dots which readily dried at room temperature. Color overprinting follows conventional silk screen multicolor printing. The stability of the combined formula was such that it could be used within 24 hours after mixing. The storage stability of the separate mixes "B" and "C" is 6 months or longer. The lower the content of aromatic solvent (e.g. xylol or cyclic naphthene) and the higher the content of petroleum wax (e.g. gilsonite, paraffin, Utah wax, etc.) the better the stability of the one package mix. In certain cases storage stability of several weeks is obtained with the high petroleum base compositions.

The ink base provided by the invention is translucent so that any color or type of dye may be added and there is accurate strength and color reproduction. There is no reaction produced between the dye and the resultant ink base which will distort the true dye or pigment color in any respect.

Any conventional inexpensive paper may be used as a transfer sheet after having been first sealed with liquid rubber or its equivalent. The silk screen frame is placed over the coated paper and inks employing the base of the invention may be pressed through the silk screen in the required pattern and onto the paper using a squeegee. No heat is involved in the application. The smoothness of the ink base enables the inks to be freely flowed through

the screen and to be clearly and distinctly impressed on the paper in the required pattern. In this manner a reverse image of the desired decal pattern is effected on the transfer sheet. This reverse image dries distinctly on the transfer sheet on ordinary exposure to air at room temperature and the transfer sheet so formed may be stored relatively indefinitely. When it is desired that this transfer sheet be used, it may be placed over the fabric on which the image is to be impressed with the impression adjacent the fabric. Application of the hot iron to the back of the transfer sheet effects an immediate transfer of the image to the fabric in a clear and distinct fashion. A positive image results which has a substantial life expectancy under ordinary usage. All colors are reproduced in perfect registration and with substantial uniformity. The combination of the waxes as emulsified by the condensed milk produces an ideal vehicle for transfer of the ink to the fabric in a clear distinct image.

Thus the ink base of the invention provides a medium enabling a cold process of effecting transfer sheets for iron-on decals which is extremely inexpensive and simple to employ. This opens up a new field of endeavor for every silk screen processer and enables him to place images, designs or any artistic creation on paper without need for expensive dies and in a manner so it can be effectively applied to fabric by a simple ironing application. The process enabled by the invention compositions expands the silk screen art to a significant degree and it is made possible by the composition provided by the invention.

The emulsions of the invention have been particularly described with reference to their use in silk screen printing. However, they may also be advantageously employed in effecting spot carbon and for similar applications. Such is comprehended as within the scope of the present invention.

I claim:

1. An oil-in-water ink emulsion adapted for silk screen printing to provide a heat releasable and heat transferable film on a transfer sheet consisting essentially of a dispersed oil phase of a wax mixture of (1) low melting, low melt-viscosity petroleum wax component, (2) intermediate melting, high melt-viscosity wax component and (3) a high melting, medium melt-viscosity wax component, said wax mixture melting gradually throughout the range from about 125° F. to about 210° F., said low melting wax component (1) melting in a range of 125–165° F. and being present in a proportion of from 41–49% by weight of the total wax present, said intermediate melting wax component (2) melting in a range of from about 142–150° F., and said high melting wax component (3) melting in a range of about 180–187° F., a liquid vegetable oil plasticizer for said wax being present in an amount of from about 24–30% of the total weight of wax and oil, a volatile petroleum hydrocarbon solvent for said plasticizer wax mixture having a boiling point of from 100–250° F. and constituting from about 44% to 52% of said oil phase, and as a stabilizing agent for said wax, plasticizer and solvent, milk protein in an amount of from about 2–8% present in said water phase, together with about 0.1 to 0.4% of alkali metal soap and 0.05 to 0.2% of borax to interact with said milk protein as the sole alkaline agents in said water phase.

2. An ink emulsion as claimed in claim 1 wherein said low melting wax component is paraffin wax which is present in an amount of from 41–49% by weight of the total wax present, said intermediate melting wax component is beeswax which is present in an amount of from 24–30% of total wax present, and said high melting wax component is carnauba wax which is present in an amount of from 24–30% of the total wax present.

3. An ink emulsion as claimed in claim 1 wherein said petroleum wax is a mixture of slack wax and ozocerite.

4. An ink emulsion as claimed in claim 1 wherein said petroleum wax is a mixture of slack wax and gilsonite.

5. An ink emulsion as claimed in claim 1 wherein said petroleum wax is a mixture of Utah wax and slack wax.

6. An ink emulsion as claimed in claim 1 wherein said intermediate melting wax component is Ghedda wax, said low melting wax component is paraffin wax and said high melting wax component is carnauba wax.

7. An ink emulsion as claimed in claim 1 wherein said high melting wax component is Ouricuri wax and said intermediate melting wax is beeswax.

8. An ink emulsion as claimed in claim 1 wherein said high melting wax component is Montan wax and said intermediate melting wax is beeswax.

9. An ink emulsion as claimed in claim 1 wherein said petroleum wax is a mixture of slack wax, Japan wax and gilsonite.

10. An ink emulsion as claimed in claim 1 wherein said wax is plasticized with linseed oil.

11. An ink emulsion as claimed in claim 1 wherein said wax is plasticized with tung oil.

12. An ink emulsion as claimed in claim 1 wherein said wax is plasticized with castor oil.

13. An ink emulsion as claimed in claim 1 wherein said wax is plasticized with a mixture of wool fat and linseed oil.

14. An ink emulsion as claimed in claim 1 wherein said petroleum hydrocarbon solvent is predominantly kerosene with a minor proportion of aromatic petroleum hydrocarbon solvent therein.

15. An iron-on decal made by silk screen printing to provide a heat releasable and heat transferable film comprising a transfer sheet printed with an oil-in-water ink emulsion consisting essentially of a wax mixture of (1) low melting, low melt-viscosity petroleum wax component, (2) intermediate melting, high melt-viscosity wax component and (3) a high melting, medium melt-viscosity wax component, said wax mixture melting gradually throughout the range from about 125° F. to about 210° F., said low melting wax component (1) melting in a range of 125–165° F. and being present in a proportion of from 41–49% by weight of the total wax present, said intermediate melting wax component (2) melting in a range of from about 142–150° F., and said high melting wax component (3) melting in a range of about 180–187° F., a liquid vegetable oil plasticizer for said wax being present in an amount of from about 24–30% of the total weight of wax and oil, a volatile petroleum hydrocarbon solvent for said plasticizer wax mixture having a boil point of from 100–250° F. and constituting from about 44% to 52% of said oil phase, and as a stabilizing agent from said wax, plasticizer and solvent, milk protein in an amount of from about 2–8% present in said water phase, together with about 0.1 to 0.4% of alkali metal soap and 0.05 to 0.2% of borax to interact with said milk protein as the sole alkaline agents in said water phase.

16. The method of making an oil-in-water ink emulsion adapted for silk screen printing to provide a heat releasable and heat transferable film on a transfer sheet comprising mixing at a temperature between 100–200° F. a wax mixture of (1) low melting petroleum wax component, (2) intermediate melting wax component and (3) a high melting wax component, said wax mixture melting gradually throughout the range from about 125° F. to about 210° F., said low melting wax component (1) melting in a range of 125–165° F. and being present in a proportion of from 41–49% by weight of the total wax present, said intermediate melting wax component (2) melting in a range of from about 142–150° F., and said high melting wax component (3) melting in a range of about 180–187° F., adding a liquid vegetable oil plasticizer for said wax and a volatile petroleum hydrocarbon solvent having a boiling point of from 100–250° F., there-

after adding milk protein in water to provide a total water content of about 41 to 50%, the milk solids content being about 6–9% of the water and adding about 0.1 to 0.4% of soap and 0.05 to 0.2% of borax to interact with said milk protein as the sole alkaline agents in said water phase.

17. A method as claimed in claim 16 wherein said milk protein in water is added in the form of condensed milk and said emulsion is pigmented.

18. A method as claimed in claim 16 wherein said milk protein in water is added in the form of reconstituted powdered milk.

19. An oil-in-water pigmented ink emulsion adapted for silk screen printing to provide discrete dots of heat transferable design on a transfer sheet consisting essentially of a dispersed oil phase consisting of a wax mixture of wide melting range petroleum wax component, and higher melting hard wax component, said wax mixture melting gradually throughout the range from about 125° F. to about 210° F., there being present a proportion of paraffin wax to provide kerosene solubility of the entire wax mixture, a liquid vegetable oil plasticizer for said wax being present in an amount from about 24% up to 30% by weight of the total weight of wax and oil and a volatile petroleum hydrocarbon solvent for said plasticizer wax mixture having a boiling point in the kerosene range and constituting about 52% to about 44% of said oil phase, a water phase, a pigment and as a stabilizing agent for said wax, plasticizer and solvent, milk protein in an amount of from about 2–8% present in said water phase.

20. An oil-in-water pigmented ink emulsion adapted for silk screen printing to provide discrete dots of heat transferable design on a transfer sheet consisting essentially of a dispersed oil phase consisting of a wax mixture of wide melting range paraffin wax component, and higher melting hard wax component selected from the group consisting of carnauba wax, Montan wax, beeswax and

mixtures of said waxes, said wax mixture gradually melting throughout the range of from about 125° F. to about 210° F., there being present a proportion of paraffin wax to provide kerosene solubility of the entire wax mixture, a liquid vegetable oil plasticizer for said wax being present in an amount from about 24% up to 30% by weight of the total weight of wax and oil and a volatile petroleum hydrocarbon solvent for said plasticizer wax mixture having a boiling point in the kerosene range, a water phase, a pigment and as a stabilizing agent for said wax, plasticizer and solvent, milk protein being present in said water phase.

21. An emulsion as claimed in claim 19 in which said solvent is kerosene containing a small proportion of xylene.

22. An emulsion as claimed in claim 19 in which there is present soap and borax each in amount less than 1% to aid suspension of the oil phase.

23. An emulsion as claimed in claim 19 wherein said pigment is a water-soluble dyestuff.

24. An emulsion as claimed in claim 19 wherein said pigment is a water-insoluble dyestuff.

References Cited in the file of this patent

UNITED STATES PATENTS

1,954,451	Lawrence	Apr. 10, 1934
1,977,680	Lawrence	Oct. 23, 1934
1,990,193	Lohmann	Feb. 5, 1935
2,044,056	Burgard	June 16, 1936
2,074,758	Reynolds	Mar. 23, 1937
2,756,874	Erickson et al.	July 31, 1956
2,961,334	Clancy et al.	Nov. 22, 1960
3,036,924	Newman	May 25, 1962

FOREIGN PATENTS

523,479	Canada	Apr. 3, 1956