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BASE VEHICLES FOR WATER-CONTENT PRINTING INK, AND WATER COLOR PRINTING INK MADE THEREWITH

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This invention relates to water-content printing inks and pertains more particularly to water-content base vehicles to be admixed with suitable pigment compositions, to produce water color printing inks.

The principal purpose of the invention is to provide a base vehicle which, when admixed with a commercial or pretreated printing ink pigment composition will provide a water-content ink capable of economical use in letter press and other conventional printing procedures, with conventional apparatus, to ensure faithful reproduction of color with transparent clarity and without the objectionable high gloss characteristic of oil-type printing inks, and with substantial reduction in setoff and strike through even on ordinary unglazed papers; which will set rapidly and dry brighter than when initially applied to paper; which may be printed in thin films and in multiple overlapping colors without crystallizing and without glare; which are water resistant, non-hygroscopic and moisture repellant, after setting, and will print over or under separately printed oil ink films, without chalking, when the oil ink films have been allowed to set so that they will not blur on contact with a water wet ink; which will not dry in the press fountains or press rolls, but will permit the machines to be washed up quickly and easily; which will print at high speeds on various types of paper, with substantial economies in the ink costs; and which, in general, will greatly improve color reproduction in the field of commercial printing, as well as in the field of graphic arts in which the esthetic qualities of the improved inks are most desirable.

A further object of the invention is to provide a number of stable combinations and sub-combinations of selected components of the base vehicle, which, as stage products in the manufacture of that vehicle, may be used in compounding the vehicle and in modifying the vehicle and the printing ink produced therewith.

The improved inks may be printed with line plates, half-tones and engraved plates, and may be used in gravure, dry-offset and silk screen processes, by conventional printing presses, on papers ranging from fine glazed or coated papers to newsprint (excepting only silicone treated or waterproofed papers), with highly advantageous results and with material economies in time, labor and ink costs.

It will be understood by the printing industry that the base vehicle and the pigment composition herein described are subject to modification and adjustment, as with conventional oil-base inks or so-called water color printing inks, according to the characteristics of the particular printing press or process, and the type of paper to be imprinted for a particular purpose; for such modifications are common practice in presswork. My new vehicle readily accepts such modifications by the addition of water or of any of the other ingredients thereof, separately or in combination or sub-combination, when necessary or desirable. Accordingly, the proportions of the base vehicle components, as hereinafter set forth, are necessarily subject to variation at the time the improved ink is supplied to the press.

For this and other reasons, I preferably prepare my ultimate base vehicle as two separate, intermixable sub-

bases: one of which is herein designated as a Dextrine Sub-Base; and the other of which is called a Casein Sub-Base. These sub-bases are intermixed in equal proportions to produce the ultimate, standard base vehicle; and the desired pigment composition is then intermixed with the vehicle in proportions ranging from 1 to 2 to 1 to 6, according to the color of the pigment, the type of paper to be printed and the printing process and equipment in which the final water-content, water color printing ink is to be used. It will be appreciated that the complete, standard base vehicle, the separate sub-bases and other combinations or stage products, or the mixed printing ink may be commercially supplied to the printer, together with separate retarders, extenders, driers and other modifiers (each incorporating one or more of the vehicle components), and instructions as to their recommended use in particular conditions.

The primary components of the novel base vehicle comprise a sulphonated vegetable oil, a casein, a vegetable dextrine, glycerin and water. The secondary, but also important components, which modify the action of the primary ingredients and also contribute, individually, to the efficacy of the improved printing inks, will be described in connection with the following explanation of the preferred formulae of the sub-bases, one of which comprises dextrine, but not casein; and the other of which comprises casein and gums but not dextrine.

The dextrine sub-base

The preferred formula for the standard dextrine sub-base comprises the following ingredients, in the proportions indicated, by weight:

	Parts
Sulphonated castor oil	105
Water	37
Tapioca dextrine	25
Glycerine	43
Sodium silicate	21½
Formaldehyde (solution)	11
Ammonium hydroxide (26°)	6½
Urea	4½
Hydrated lime	2½
	256

The casein sub-base

The preferred formula for the standard casein sub-base comprises the following components in the proportions stated:

	Parts
Sulphonated castor oil	72
Water	127 5/16
Sodium caseinate	3⅞
Glycerine	18
Sodium silicate	6 15/16
Formaldehyde (solution)	9 15/16
Ammonium hydroxide (26°)	7 15/16
Urea	4⅞
Hydrated lime	1 3/16
Gum arabic	3⅜
Gum tragacanth	1½
Guar gum	trace
	256

In the preparation of each of the main sub-bases, it is preferred that combinations and sub-combinations of selected components be first compounded as stage products and then intermixed; and such combinations or stage products may be stored as stable compositions, and subsequently used as modifiers of the completed ink formula-

tion, when modification is desired for particular conditions.

For example, the following sub-combinations are preferably prepared for the dextrine sub-base:

Combination I

Sub-combination 1:	Parts
Dextrine	37
Glycerine	46
Sodium silicate	21
Water	5
Formaldehyde (solution)	1
Ammonium hydroxide (26°)	1
Total	111

Sub-combination 2:	Parts
Water	35
Hydrated lime	6
Ammonium hydroxide (26°)	6
Formaldehyde (solution)	1
Total	48

30 parts of sub-combination 1, mixed with 5 parts of sub-combination 2, and 10 parts of sulphonated castor oil produce Combination I. This combination or stage product is preferably prepared by first dissolving the dextraine powder in glycerine at boiling temperature, then allowing the solution to stand until cooled (preferably 12 to 16 hours); adding, at room temperature, a mixture of sodium silicate, glycerine, formaldehyde solution, ammonium hydroxide and water (sub-combination 3, below), and stirring to form a viscous caramelized, gummy varnish which may be stored as sub-combination 1, above; then adding, while stirring, the sulphonated oil and finally 5 parts of sub-combination 2, to produce a softer, smoother and less viscous gummy paste, as another stage product (Combination I).

Combination II

Sub-combination 3:	Parts
Sodium silicate	18
Glycerine	8
Water	4
Formaldehyde (solution)	1
Ammonium hydroxide (26°)	1
Total	32

Sub-combination 4:	Parts
Glycerine	12
Urea	6
Water	5
Formaldehyde (solution)	1
Total	24

Sub-combination 4 is preferably produced by mixing the urea in heated glycerine, until completely dissolved, and then adding the formaldehyde and water, while the solution is cooling.

10 parts of sub-combination 3, mixed with 10 parts of sub-combination 4 and 20 parts of sulphonated castor oil produce Combination II.

Combination III

Then, when 40 parts of Combination I, 12 parts of Combination II and 48 parts of sub-combination 2 are intermixed, another utilizable Combination III is formed, to be combined with the Combination IV next to be described, in forming the Dextrine Sub-Base.

Combination IV

Sub-combination 5:	Parts
Sulphonated castor oil	60
Water	24
Formaldehyde (solution)	5
Ammonium hydroxide (26°)	5
Hydrated lime	2
Total	96

Then, when 96 parts of sub-combination 5 is mixed with 60 parts of Combination II, still another stage product, Combination IV, is formed; and a mixture of 100 parts of Combination III and 156 parts of Combination IV produces the Dextrine Sub-Base, as aforesaid.

The Casein Sub-Base is composed of the stage product combinations now to be described.

Combination V

	Parts
Water	17⅛
Sulphonated castor oil	3
Glycerine	3½
Gum arabic	3⅜
Sodium caseinate	⅜
Ammonium hydroxide (26°)	¾
Formaldehyde (solution)	15/16
Urea	⅜
Sodium silicate	⅝
Guar gum	1/16
Total	30

Combination VI

	Parts
Water	39⅜
Sulphonated castor oil	3
Glycerine	7
Ammonium hydroxide (26°)	2
Formaldehyde (solution)	3 1/16
Urea	1⅞
Sodium silicate	1 11/16
Gum tragacanth	1½
Total	60

Combination VII

	Parts
Water	61½
Sulphonated castor oil	43½
Glycerine	3
Sodium caseinate	3⅝
Ammonium hydroxide (26°)	2 7/16
Formaldehyde (solution)	3 9/16
Urea	1 9/16
Sodium silicate	1
Total	120

Combination VIII

	Parts
Water	2
Glycerine	1
Ammonium hydroxide (26°)	⅝
Formaldehyde (solution)	⅝
Urea	⅜
Sodium silicate	1⅛
Hydrated lime	⅜
Total	6

The Casein Sub-Base is produced by mixing said Combinations V, VI, VII and VIII, in the total proportions stated with 40 parts of Combination IV above.

In preparing Combinations V and VII, the following procedure is preferably followed to dissolve the sodium caseinate and initially mix it with some of the other ingredients of those stage products: place the sodium caseinate powder in water (in proportions of 4 ounces to 1 pound) and soak while heating and stirring until dissolved; add a dilute solution of formaldehyde and ammonium hydroxide and stir at a temperature of approximately 160° F., to completely liquefy the mixture; then let stand until cool, adding cold water to expedite cooling below room temperature; then add a dilute solution of formaldehyde and another pound of water, stirring all room temperature; add about 4 ounces of sulphonated castor oil, while stirring, to thicken and lengthen the

solution; and finally add and stir in about 6 ounces of urea, 18 ounces of a dilute solution for formaldehyde and ammonium hydroxide, and 48 ounces of sulphonated castor oil.

Complete base vehicle

The standard base vehicle consists of a mixture of the Dextrine Sub-Base and the Casein Sub-Base, in equal proportions, and thus comprises the following ingredient proportions:

	Parts	Approximate Percentage
Sulphonated castor oil	177½	34.5
Water	166 9/16	32.5
Glycerine	60⅛	12
Tapioca dextrine	25	5
Sodium silicate	28⅛	5.4
Formaldehyde (solution)	19⅞	3.8
Ammonium hydroxide (26°)	12 9/16	2.4
Urea	9⅜	1.8
Sodium caseinate	3⅞	0.8
Hydrated lime	3 5/16	0.7
Gum arabic	3⅜	0.7
Gum tragacanth	1½	0.3
Guar gum	1/16	Trace
Total	512	

The pigment composition with which this base vehicle is combined to produce the water-content, water color ink may be a commercial ink, as supplied to printers by ink manufacturers, provided its composition is compatible with the base vehicle or can be slightly modified to be compatible before it is mixed with the water-content base vehicle. A commercial ink comprising a color pigment ground in glycerine is satisfactory without modification; but a pigment composition containing a substantial part of glucose or alcohol is not satisfactory without modification.

The pigment composition may be mixed with the base vehicle in proportions ranging from 1 to 2 to 1 to 6, as aforesaid, according to the color effect desired, the paper to be used and the characteristics of the press, as determined by the experience of the printer.

Although the proportions of the dextrine component and the casein component in the complete base vehicle are relatively small, these components are very active in the mixture and are critical (particularly the casein) in achieving the beneficial results outlined above. The vegetable dextrine, in blended association with the water soluble, vegetable gums (particularly gum tragacanth), the urea and the glycerine, specified in the formulation of the vehicle provide softness and tackiness with slow drying qualities to the paste-like, viscous vehicle; whereas, the casein component, in association with formaldehyde and gum arabic contributes to the rapid drying and hard setting of the ink, in a firm, water-resisting, thin film, as well as affording adhesive properties to the ink, in the presence of the emulsifying sulphonated vegetable oil and the urea components. Thus, certain components tend to counteract the effect of other components, and a desired balance may be obtained by varying the proportions of the mutually counteracting ingredients.

The sulphonated oil not only emulsifies the dextrine, forming a pulpy and viscous jelly, but also acts as a plasticizer and extender of the ink, in the presence of water which, it will be observed, constitutes at least 30 percent of the vehicle, and is also a critical component of the base vehicle, and of the resulting printing ink which should have a water content of at least 15 percent. Water may be added to the finished ink whenever it is desired to thin the ink or to replace loss by evaporation.

The water serves as a neutral vehicle and extender for the other components of the base vehicle, and, in the minimum proportion stated, contributes substantially to the economy of the water-content printing ink. It is not a printing element, but it is essential in dispersing the ink pigments and in the formulation and application of the ink in press operation. The evaporation of the water, by friction and heat of the printing press desirably increases the humidity of the pressroom. It is thus a necessary component of the base vehicle, and not merely a solvent.

The formaldehyde solution may be a commercial grade as marketed, for example, by the Du Pont Company. In its combinations and sub-combinations, this component hardens, tempers and waterproofs the casein as the ink film dries; it assists in rejecting moisture after the film has dried; and it affords a suspending medium for urea.

The urea acts as a softener and retarder counterbalancing too rapid drying; it tends to prevent compacting or "rubberizing" of the casein solution; it assists in causing the ink film to penetrate paper; and it acts as a preservative.

The glycerine dissolves the ink pigment and ensures its dispersal in the water content, and acts as a humectant. Its proportioned content should be kept relatively low, to avoid excessive hygroscopic action, and undue slipperiness of the ink.

The sodium silicate acts as adhesive binder, and tends to dehydrate the glycerine and the sulphonated oil.

The ammonium hydroxide assists in degreasing and diluting the glycerine and the sulphonated oil, and in ensuring bright colors upon drying of the ink film on paper.

The hydrated lime also acts as a degreaser; it softens the dextrine, adds bulk and contributes to a dense ink film when desired; it acts as a binder and stabilizer; it does not dissolve or emulsify, but tends to precipitate from the mixture, so that the base vehicle, and any separate combinations or sub-combinations containing hydrated lime should be shaken before using.

The vegetable gums serve as adhesives and driers, gum arabic being a faster drier tending to produce a hard film, whereas gum tragacanth is a slower drier and tends to form a softer film; and guar gum being intermediate in its action. These gums are powerful ingredients, and small proportions of them serve their purposes.

The properties of the aforesaid components, used alone or in sub-combinations, are valuable in securing particular results desired in particular conditions. In the preferred formula of the new vehicle base, the properties of certain ingredients counterbalance the properties of other ingredients to provide a balanced composition which may readily be modified by adding small proportions of appropriate, compatible components or sub-assemblies to obtain the desired affect. For example, if a slower drying ink is desired, as in taking printers' proofs, the proportions of gum arabic and gum tragacanth should be interchanged, in the formula for the complete base vehicle. Any such modifications or adjustments are freely reversible, so that the base vehicle and the resulting printing inks are very flexible in use and performance.

I am aware that so-called water color inks have heretofore been used in printing, but such inks have not incorporated water as a vehicle or other component. Such inks invariably comprise an excessive proportion of pigment and glycerine (with glucose) with the result that the very dense ink films loose transparency when overprinted, and become chalky after drying; and such inks are unsuitable for half-tone printing, because of poor registration due to the slippery characteristics of the glycerine. Such inks are not water-content inks; their use is substantially limited to rubber or other specialized plates or rollers; and they are incapable of achieving the results obtained by my novel water-content inks, in general printing, or limited printing.

Water-content, water color inks incorporating my novel base vehicle permit more color films to overlap, without loss of transparency or translucency, than any printing ink heretofore available. Each overprinted film opens up the previously printed film and amalgamates with it, to ensure clear but non-glaring color reproductions simulating hand-applied artists' water color paints.

Although I prefer to use sulphonated castor oil and

tapioca dextrine in compounding the base vehicle, it will be understood that peanut oil or olive oil may be combined with the castor oil, and that corn dextrine may be used with, or in place of, the tapioca dextrine. Granular casein may also be substituted for sodium caseinate. It will also be understood that the proportions of the ingredients of the preferred base vehicle are subject to variation within reasonable limits, depending upon the results desired and the nature of the press and the paper to be imprinted; but the water content of the vehicle should be at least 30 percent, in any formulation; and the water content of the final printing ink should be at least 15 percent, as aforesaid.

When granular casein is used as a substitute for sodium caseinate, the procedure for preparing a preliminary casein subcombination is preferably as follows: 4 ounces of the granular or crystal casein is soaked and stirred in 1 pound of cool water for about thirty minutes; one-quarter ounce of ammonium hydroxide (26°) is then added and is stirred in while heating the water to a temperature of approximately 160° F., to dissolve the casein; the liquified mass is then permitted to stand and cool, and 1 pound of cold water is slowly added while cooling below room temperature; 6 ounces of dilute formaldehyde solution (1 part original formaldehyde solution plus 5 parts of water) is next added slowly while stirring; then 1 pound of water is added to the cool, liquefied mass, while stirring at room temperature, to furnish a thin, sticky and fast drying liquid, in which the casein is completely dissolved.

In order to provide a stage product equivalent to combination VII above, for storage and modifying use, the following mixtures or components are added to the foregoing casein solution: six ounces of a mixture of 4 parts urea, 8 parts glycerine, 4 parts formaldehyde solution and 20 parts water; 18 ounces of a mixture of 1 part formaldehyde solution, 1 part ammonium hydroxide (26°) and 5 parts water; six ounces of a dilute formaldehyde solution, composed of 5 parts of water and 1 part of the original formaldehyde solution; 2 ounces of a mixture of 9 parts sodium silicate, 4 parts glycerine and 3 parts of the aforesaid dilute formaldehyde solution; and 48 ounces of the sulphonated castor oil.

It will be appreciated that the ink or the base vehicle may be reconstituted by adding water to compensate for any loss due to evaporation or chemical action within the composition, after long standing or storage. Such additional water in no wise impairs the quality of my improved water-content printing ink. Water may also be added during the printing operation, wherever desired. Such restoration of ordinary printing inks, after long standing, or in press operation, is not possible.

I claim:

1. A base vehicle for water-content, water color printing inks consisting of the following components in the following approximate proportions by weight: sodium caseinate, 0.8%; tapioca dextrine, 5%; sulphonated castor oil, 34.5%; water, 32.5%; glycerine, 12%; formaldehyde solution, 3.8%; ammonium hydroxide, 2.4%; urea, 1.8%; and hydrated lime, 0.7%.

2. A base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: sulphonated castor oil, 34.5%; water, 32.5%; glycerine, 12%; tapioca dextrine, 5%; sodium silicate, 5.4%; formaldehyde solution, 3.8%; ammonium hydroxide, 2.4%; urea, 1.8%; sodium caseinate, 0.8%; hydrated lime, 0.7%; gum arabic, 0.7%; gum tragacanth, 0.3%; and guar gum, trace.

3. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: water, 35 parts; hydrated lime, 6 parts; ammonium hydroxide, 6 parts; and formaldehyde solution, 1 part.

4. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: glycerine, 46 parts; dextrine, 37 parts; sodium silicate, 21 parts; water, 5 parts; formaldehyde solution, 1 part; and ammonium hydroxide, 1 part.

5. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: sulphonated castor oil, 60 parts; water, 24 parts; formaldehyde solution, 5 parts; ammonium hydroxide, 5 parts; and hydrated lime, 2 parts.

6. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: sodium silicate, 18 parts; glycerine, 8 parts; water, 4 parts; formaldehyde solution, 1 part; and ammonium hydroxide, 1 part.

7. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: water, 17⅛ parts; sulphonated castor oil, 3 parts; glycerine, 3½ parts; gum arabic, 3⅜ parts; sodium caseinate, ⅜ part; ammonium hydroxide, ¾ part; formaldehyde solution, $^{15}/_{16}$ part; urea, ⅜ part; sodium silicate, ⅝ part; and guar gum, 1/16 part.

8. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: water, 39⅜ parts; sulphonated castor oil, 3 parts; glycerine, 7 parts; ammonium hydroxide, 2 parts; formaldehyde solution, 3 1/16 parts; urea, 1⅞ parts; sodium silicate, $1^{11}/_{16}$ parts; and gum tragacanth, 1½ parts.

9. A stage product in the manufacture of a base vehicle for water-content, water color printing inks, consisting of the following components in the following approximate proportions by weight: water, 61½ parts; sulphonated castor oil, 43½ parts; glycerine, 3 parts; sodium caseinate, 3⅝ parts; ammonium hydroxide, 2 7/16 parts; formaldehyde solution, 3 9/16 parts; urea, 1 9/16 parts; and sodium silicate, 1 part.

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