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Roccheggiani et al.

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[54] **PRINTING FLUID**

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[63] Continuation of Ser. No. 424,220, Jan. 8, 1965, abandoned.

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[51] **Int. Cl.** **C08g 51/24,** C08g 51/66

[58] **Field of Search** 260/29.4, 69, 70; 162/126, 162/134, 162, 166, 167; 8/7, 18, 82, 85, 76; 106/20, 22; 7/15, 38

[56] **References Cited**

UNITED STATES PATENTS

2,556,902	6/1951	Chambers et al.	260/29.4
2,699,435	1/1955	Auten et al.	260/69
2,730,446	1/1956	Hutchins	162/162
3,275,605	9/1966	Eastes et al.	260/70

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[57] **ABSTRACT**

Aqueous, low-viscosity, printing fluids comprising an aqueous solution of (A) a thermosetting polyhydroxy-polyalkylenepolyurea-formaldehyde resin condensate and (B) a water-soluble dye which is compatible with the resin condensate. These printing fluids are useful in high speed paper printing processes.

9 Claims, No Drawings

PRINTING FLUID

This application is a continuation of Ser. No. 424,220, filed Jan. 8, 1965, now abandoned.

This invention pertains to novel printing fluids; more particularly, this invention relates to certain aqueous printing fluids of certain mixtures of thermosetting resins and particular dyes suitable for printing unsized webs at printing velocities, for example, up to about 5,000 ft./min. and over. The printed products obtained by printing with the novel printing fluids are within the purview of this invention.

In a majority of prior-art rotogravure processes pigmented printing fluids of high vapor pressure solvents have been used. These fluids contain dispersed particular matter of great hiding power. Particles dispersed within these fluids give the tinctorial strength needed for printing when these fluids are deposited on the surface of the printed web and the solvent removed thereafter.

While the final print quality of these fluids is often excellent, the process possesses inherent limitations such as the velocity at which the web may be printed as well as the rate of solvent removal from the pigmented fluids. Needless to say, the many dangers inherent in using high vapor pressure solvents are considerable.

Other prior-art shortcomings, in comparison with this process, are the life span of the rotogravure roll or intaglio surface because the pigmented particular materials abrade the roll surface in places of contact with another surface such as the printing nip, and doctor blades.

Still other shortcomings found in prior art rotogravure printing are the higher viscosities of printing fluids. The viscosity, coupled with the abrasive nature of the fluid, illustrates why rotogravure rolls are short-lived in comparison with this process. Additionally, the high viscosity of the fluid prevents the printing process from running at high speeds. For example, at high speeds the tackiness of the prior-art fluids would cause fiber "picking" or removal from the web and at still higher viscosities cause the paper to wrap itself around the printing surface. This phenomenon is avoided by reducing the viscosity of the printing fluid by adding solvent.

Therefore, it is obvious that any change in one property of the fluid will significantly alter other properties of the fluid if the nature of the prior art system is significantly changed to obtain improved results.

It has now been found that a completely new and unobvious approach in printing fluids does overcome most of the prior-art shortcomings and allows the printing operations to be carried out at web velocities up to about 5,000 ft./min. and higher or a web velocity of about a mile per minute at a cost substantially lower than achievable by any prior-art processes.

The novel printing fluid suitable for rotogravure printing at web velocities up to about 5,000 ft./min. comprises an aqueous solution of a thermosetting resin of the polyhydroxy-polyalkylene-polyurea-formaldehyde condensate type, a dye compatible with said resin, said dye and resin mixture having a stability of from about one hour to in excess of 4 months and a transference value of from about 0 to about 4, and a viscosity at 77°F of about 20 cps.

This printing fluid, as further amplified herein, is suitable for rotogravure intaglio printing of papers having an absorbency time of 600 sec./0.01 ml of water. The preferred papers have absorbency properties as depicted in the following table:

TABLE

Types of Paper	ABSORBENT PAPERS Most Preferred	More Preferred	Preferred
Multi-Ply Toilet/Facial Tissues			
Basis Weight lb/ream	9.2 - 10.7	7.5 - 11.5	5.0 - 15.0
Absorbency second/0.10 ml	0 - 10	0 - 15	0 - 180
Single-Ply Toilet Tissue			
Basis Weight lb/ream	11.5 - 14.0	9.0 - 16.0	7.0 - 20.0
Absorbency sec/0.01 ml	0 - 60	0 - 120	0 - 300
Single-Ply - Towel/Wiper			
Basis Weight—lb/ream	20.0—36.0	11.0—40.0	10.0—50.0
Absorbency—sec./0.10 ml	0—60	0—360	0—600
Multi-Ply Towel/Wiper			
Basis Weight—lb/ream	9.0—20.0	8.0—21.0	5.0—25.0
Absorbency—sec/.01 ml	0—60	0—300	0—600
Single-Ply Napkin			
Basis Weight—lb/ream	12.0—15.5	9.0—19.0	6.0—25.0
Absorbency—sec/0.01 ml	0—100	0—360	0—600
Multi-Ply Napkin			
Basis Weight—lb/ream	9.7—11.2	7.0—15.0	5.0—20.0
Absorbency—sec/0.10 ml	0—300	0—600	0—600

Basis weight is expressed in pounds per 24 × 36 inches × 480 sheet ream (2,880 square ft.).

Absorbency is expressed in seconds as the time required for the paper specimen to absorb a specified volume of distilled water. The area of each specimen (obtained from a retail case) is to be no less than 9 square inches, cut to 3 × 3 inches. The specimen to be tested will be suspended in a suitable frame to provide a flat, undistorted surface with no contact on either side of the specimen with any other surface or material. With the specimen thus prepared, the specific volume of water in a single drop will be lowered by appropriately divisioned pipette to the surface of the specimen. Tim-

ing begins as the water drop touches the specimen and ends with complete absorption - defined as the instant at which the water on the surface fails to reflect light.

For single-ply tissue and/or napkins . . . 0.01 ml H_2O

For all others . . . 0.10 ml H_2O

Samples from each case will be from no less than 10% of the retail package contained therein. Each individual test will be the result of three drops/side, reporting the 6-drop average as the individual test result. The average of these tests will represent the absorbency.

The test described above conducted under atmospheric conditions controlled to 75 ± 2°F and 60 ± 2% R.H.

The resin as disclosed herein is obtained by a process for preparing polyhydroxypolyalkylenepolyurea-formaldehyde condensates which comprises reacting between about 0° and 100°C, in the presence of water, epichlorohydrin and an alkylene polyamine having two to three carbon atoms in the alkylene portion thereof in a mole ratio from 1 : 1 to 1.4 : 1 until an aqueous solution of the resulting polyhydroxypolyalkylenepolyamine at a concentration of about 46% has a viscosity from J to Z_7 at 25°C. on the Gardner-Holdt scale, reacting said polyhydroxypolyalkylenepolyamine with urea between 100° and 200°C in a ratio from 0.5 : 1 to 1.8 : 1 of urea per —NH— group of said polyhydroxypolyalkylenepolyamine until an aqueous 45% solution of the resulting polyhydroxypolyalkylenepolyurea has a viscosity from B to Z_3 at 25°C on the Gardner-Holdt scale, and reacting said polyhydroxypolyalkylenepolyurea with formaldehyde in a solution at a pH between 7 and 9.5. (These condensates have been further described in U.S. Pat. No. 2,699,435.)

In order to render the present resin acceptable for printing purposes the resin must be modified by acidic catalysts compatible with the dye-resin solutions. Examples of such acid catalysts are such as acetic acid, lactic acid, glycolic acid, diglycolic acid, citric acid, phosphoric acid, hydrochloric acid, ammonium chloride, etc.

Further, to improve fluid stability, particularly at low resin-to-dye ratios, fluid additives are included; these are exemplified by compounds such as formaldehyde, methyl alcohol, glyoxal, glycols such as ethylene (low molecular-weight polyethylene glycol) and propylene glycol, glycol ethers such as cellosolve and Carbitol; formamide, dimethylformamide, polyvinyl pyrrolidone, tetrahydrofurfuryl alcohol, dimethyl sulfoxide, etc.

Urea is also added to the present fluid for dye solubilizing and formaldehyde scavenging. If problems exist with fluid affinity for gravure rolls, which are generally chrome plated, surface-active agents may be added. Examples of these are nonionic surface-active agents such as nonylphenoxypoly(ethyleneoxide) and others obtainable from Atlas Chemical Corp. such as the Atmos, Atmul, and Tween Series of non-ionics.

The resin in solution must also exhibit non-dilatant viscosity characteristics. For purposes of this invention, the described condensates are also limited by the viscosity considerations as set out herein.

The water-soluble dyes useful in the novel fluid are generally those with anionic characteristics, i.e., bearing an opposite charge to the resin. Although the combination of a cationic resin and an anionic dyestuff is basically incompatible, this difficulty can be overcome by using an amount of resin in excess of the stoichiometric ratio. For example, most water-soluble cationic thermosetting resins may be made compatible with direct, acid and reactive dyes.

This stabilized solution, it is believed, in turn coacts by curing on the fibers in the web and the degree of this reaction is measured by a transference value.

As there are an untold number of dyes and each dye, it has been found, reacts unpredictably vis-a-vis the particular resin, only a certain family of dyes will be operative in this process. However, since the concept of using a particular water-soluble thermosetting resin with a particular dye is novel from the stability aspect as well as the transfer value aspect, many dyes are eliminated on the basis of the first ground as well as on the second. The tests designed to delineate the acceptable dyes from those failing in the instant fluids are set out below and fully discussed. Again, it is stressed that not all dyes meet the first two requirements and that predictability is impossible to establish beforehand. Moreover, in order for the dye to be acceptable, it must be used in quantities such as will establish an acceptable print. Again, this property relates to stability as the dye affects the fluid stability if the dye is present in considerable amounts. In other words, for each particular resin-dye combination a direct relationship exists between fluid stability and the ratio of resin non-volatile solids (N.V.S.) to dye, i.e., stability is adversely affected as the resin to dye ratio decreases.

Fluid stability at room temperature (77°F) is herein defined as the period of time intercurring between the manufacture of a fluid and the appearance of physical-chemical changes that would adversely affect operability. These changes usually take place over a period of time and the limiting factors from the standpoint of fluid utilization are the following: A ± 25% change in fluid viscosity from the original value and a departure from the initial one-phase solution.

Stability is measured on an arbitrary scale defined from most preferred fluids as A, signifying a stability of one month or more, for preferred fluids as B, signifying a stability of 1 week to a month, for useable fluids as C, the stability ranging from one hour to one week and for unacceptable fluids as 0, the stability being one hour or less or complete incompatibility in fluid components.

Fluid stability as herein defined is also indicative of "shelf life" or "storage life". Storage life, as defined by the Packaging Institute in the *Glossary of Packaging Terms*, 2nd ed., Riverside Press, Essex, Conn., 1955, "is the period of time during which a packaged product can be stored under specific temperature conditions and remain suitable for use. Sometimes called shelf life."

Even if a proper amount of dye can be dissolved in the solution it may not be acceptable because of the bleeding in water "or transfer value test."

The novel printing fluids can also be cleaned which is hardly possible with the pigmented printing fluids since filtering or centrifugation would remove pigment tinctorial material. This property of fluid gives rise to a recirculating system as, in the case of loosely-bonded absorbent papers, the paper dust and loose fibers must be removed from the fluid in order not to overload the system with particulate materials. Therefore, the need for a low-viscosity aqueous solution is important as these solutions can be easily cleaned or separated from impurities such as by centrifugation. This viscosity criterion is of importance because the impurities are re-

moved by cleaning means such as those based upon differences in specific gravity. Consequently, dust-laden webs as well as loosely-bonded webs can be printed by means of this fluid because they are cleanable.

Transference, as previously mentioned, relates to the ability of the printed area to resist water washing or bleeding after the resin has cured to the thermosetting state.

Transference solutions establishing the standard values for the different resin dye mixtures and classifying acceptable fluids are given below:

Transfer is herein defined as the amount of tinctorial material removed from the original colored area by the addition of distilled water and transferred to either an unprinted area of the same substrate or onto another substrate when physical contact is established.

Transfer rating scale:

0 - No noticeable transfer
1 - Very slight (barely noticeable) transfer
2 - Slight transfer
3 - Moderate transfer
4 - Heavy transfer
5 - Very heavy transfer

The transfer rating scale is based on the intensity of the color removed when compared with the intensity of the original colored area.

Transfer rating is by definition 0 as a result of carrying out the following experiment: 2 g. of C.I. Direct Blue 1 dyestuff (DuPont Pontamine Sky Blue 6 BX) are dissolved in 50 ml of distilled water heated to 130°F and transferred into 50 g. of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (30% N.V.S.), U.S. Pat. No. 2,699,435 (Example 2, appropriately adjusted for its N.V.S. content) Uformite 700 (Rohm & Haas) with agitation. Subsequently, 3 g. of NH_4Cl are added to the dye-resin solution and mixing is continued until the catalyst is completely dissolved. Using a 100 microliter pipette, three-hundredths of one ml (0.3 ml) of fluid is placed on a No. 1 Whatman filter paper and dried (cured) for 1 hour in an oven at 230°F. The colored portion of the filter paper is then immersed for 5 seconds in distilled water, the excess water is removed by contacting any absorbent medium, and finally the damp test sample is sandwiched between two two-layer pads of No. 1 Whatman filter paper. A two-pound weight is placed on the top of the filter pad and remains there for at least 10 hours, after which time the sample is removed and the 2 filter surfaces in contact with the test sample upon examination exhibit no noticeable transfer.

Transfer rating is by definition 1 as a result of carrying out the following experiment: 2 g. of C.I. Direct Blue 1 dyestuff (DuPont Pontamine Sky Blue 6BX) are dissolved in 50 ml of distilled water heated to 130°F and transferred into 50 g. of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (30% N.V.S.), U.S. Pat. No. 2,699,435, Uformite 700 (Rohm & Haas) with agitation. Subsequently, 3 g. of NH_4Cl are added to the dye-resin solution and mixing is continued until the catalyst is completely dissolved. Using a 100 microliter pipette, three-hundredths of 1 ml (.03 ml) of fluid is placed on a No. 1 Whatman filter paper and dried (cured) for 10 minutes in an oven at 230°F. The colored portion of the filter paper is then immersed for five seconds in distilled water, the excess water is removed by contacting any absorbent medium, and finally the damp test sample is sandwiched between two two-layer pads of No. 1 Whatman filter paper. A 2-pound weight is placed on the top of the filter pad and remains there for at least 10 hours after which time the sample is removed and the two filter surfaces in contact with the test sample upon examination exhibit a very slight (barely noticeable) transfer.

Transfer rating is by definition 2 as a result of carrying out the following experiment: 2 g. of C.I. Direct Blue 1 dyestuff (DuPont Pontamine Sky Blue 6 BX) are dissolved in 50 ml of distilled water heated to 130°F and transferred into 50 g. of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (30% N.V.S.) U.S. Pat. No. 2,699,435, Uformite 700 (Rohm & Haas) with agitation. Subsequently, 0.5 g. of NH_4Cl is added to the dye-resin solution and mixing is continued until the catalyst is completely dissolved. Using a 100 microliter pipette, three-hundredths of 1 ml (.03 ml) of fluid is placed on a No. 1 Whatman filter paper and dried (cured) for 60 minutes in an oven at 230°F. The colored portion of the filter paper is then immersed for 5 seconds in distilled water, the excess water is removed by contacting any absorbent medium, and finally the damp test sample is sandwiched between two two-layer pads of No. 1 Whatman filter paper. A 2-pound weight is placed on the top of the filter pad and remains there for at least 10 hours, after which time the sample is removed and the two filter surfaces in contact with the test sample upon examination exhibit a slight transfer.

Transfer rating is by definition 3 as a result of carrying out the following experiment: 2 g. of C.I. Direct Blue 1 dyestuff (DuPont Pontamine Sky Blue 6 BX) are dissolved in 50 ml of distilled water heated to 130°F and transferred into 50 g. of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (30% N.V.S.), U.S. Pat. No. 2,699,435, Uformite 700 (Rohm & Haas) with agitation. Subsequently, 0.5 g. of NH_4Cl is added to the dye-resin solution and mixing is continued until the catalyst is completely dissolved. Using a 100 microliter pipette, three-hundredths of one ml (0.3 ml) of fluid is placed on a No. 1 Whatman filter paper and dried (cured) for 30 minutes in an oven at 230°F. The colored portion of the filter paper is then immersed for 5 seconds in distilled water, the excess water is removed by contacting any absorbent medium, and finally the damp test sample is sandwiched between two two-layer pads of No. 1 Whatman filter paper. A 2-pound weight is placed on top of the filter pad and remains there for at least ten hours, after which time the sample is removed and the two filter surfaces in contact with the test sample upon examination exhibit a moderate transfer.

Transfer rating is by definition 4 as a result of carrying out the following experiment: 2 g. of C.I. Direct Blue 1 dyestuff (DuPont Pontamine Sky Blue 6 BX) are dissolved in 50 ml of distilled water heated to 130°F and transferred into 50 g. of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (30% N.V.S.), U.S. Pat. No. 2,699,435, Uformite 700 (Rohm & Haas) with agitation. Subsequently, 0.5 g. NH_4Cl is added to the dye-resin solution and mixing is continued until the catalyst is completely dissolved. Using a 100 microliter pipette, three-hundredths of 1 ml of fluid is placed on a No. 1 Whatman filter paper and dried (cured) for 15 minutes in an oven at 230°F. The colored portion of the filter paper is then immersed for 5 seconds in distilled water, the excess water is removed by contacting any absorbent medium, and finally the

damp test sample is sandwiched between two two-layer pads of No. 1 Whatman filter paper. A 2-pound weight is placed on the top of the filter pad and remains there for at least 10 hours, after which time the sample is removed and the two filter surfaces in contact with the test sample upon examination exhibit a heavy transfer.

Transfer rating is by definition 5 as a result of carrying out the following experiment: 2 g. of C.I. Direct Blue 1 dyestuff (DuPont Pontamine Sky Blue 6 BX) are dissolved in 50 ml of distilled water heated to 130°F and transferred into 50 g. of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (30% N.V.S.), U.S. Pat. No. 2,699,435 Uformite 700 (Rohm & Haas) with agitation. Subsequently, the dye-resin solution pH is adjusted to 10 by addition of 20 drops of saturated NaOH solution and mixed until the catalyst is completely dissolved. Using a 100 microliter pipette, three-hundredths of 1 ml of fluid is placed on a No. 1 Whatman filter paper and sample remains uncured (not oven dried). The colored portion of the filter paper is then immersed for 5 seconds in distilled water, the excess water is removed by contacting any absorbent medium, and finally the damp test sample is sandwiched between two two-layer pads of No. 1 Whatman filter paper. A 2-pound weight is placed on the top of the filter pad and remains there for at least 10 hours, after which time the sample is removed and the two filter surfaces in contact with the test sample upon examination exhibit a very heavy transfer.

For the process to be operative at the high-web velocities such as above 5,000 ft./min. the viscosity of the fluid must be kept within certain limits. At lower web velocities the viscosity may be higher such as about 20 cps, but again, a more viscous fluid picks up more fiber and may be harder to clean and for this reason is not desirable. For purposes of this process viscosities below 15 cps are preferred. The preferred range of viscosity for the fluid is of from about 3 cps to 10 cps while the most preferred range is about 3 cps to about 7 cps at 77°F.

In the instant case procedure for determination of liquid viscosities by the Cannon-Fenske Routine Viscometer was used. Equipment needed for viscosity determination includes a constant temperature bath, a timer and the proper size Cannon-Fenske Routine Viscometer tube. Size 50 tube is recommended for a range of 0.8 to 3.2 centistokes, size 100 tube for 3 to 12 centistokes, size 150 tube for 7 to 28 centistokes and size 200 tube for 20 to 80 centistokes.

The bath temperature is maintained at 25.0°C ± 0.1°C. The viscosity in centipoises is then calculated by multiplying the centistoke viscosity by the liquid density at 25°C. The liquid density at 25°C is calculated by the following equation: Density of liquid at 25°C = (sp.g. at t°F) (dens. water at 60°F)

$$\frac{\text{Dens. water at } 25^\circ\text{ C.}}{\text{dens. water at } t\ ^\circ\text{F.}} = (.00610)\frac{(\text{sp. g. @ } t\ ^\circ\text{F.})}{(\text{dens. water at } t\ ^\circ\text{F.})}$$

The above procedure as employed herein is discussed by M. R. Cannon in Ind. Eng. Chem., Anal., Ed., 10,297 (1938).

In another aspect the present fluid differs from those of prior art, namely, surface tension. While most of the prior art fluids are designed with low surface tension characteristics to allow the wetting of the roll by the viscous fluid presently defined fluids are operable at high-surface tension values because low viscosity fluid wets the intaglio surface at acceptable rates. Depending on the degree of surface wetting the surface tension may be varied by adding minor amounts of wetting agents to give the best results. The preferred values are below 50 dynes/cm and below the surface value of pure water (72 dynes/cm). An acceptable range is of from about 30 dynes/cm to about 60 dynes/cm. The surface tension is measured by means of Cenco-duNouy tensiometer.

In comparing the print obtained by means of the prior art pigmented rotogravure inks with the print obtained by the novel fluid the following differences exist. The prior art inks are opaque, i.e., they have considerable hiding power (impervious to the rays of light). On the other hand, the present dyes are transparent although these may be colored. The color value adjustment in prior art is obtained by adding white pigment and coloring. In the present fluids it is performed by preparing a different fluid with a different dye concentration. In practicing this invention, the white pigment is not needed and its place is taken by the color of the substrate, i.e., the color of fibers which are for the most part white for bleached pulp. Consequently a component previously required in a rotogravure ink is now eliminated. Of course, the printing of colored base sheets necessitates the use of colors that, upon becoming deposited on the base sheets will give the needed color, e.g., a blue base sheet must be printed with yellow dye-resin solution to obtain green color.

Besides the above factors which contribute to the acceptance of the present fluids, the cost factor is an equally important consideration herein. For example, the cost as well as the necessity of pigment and grinding of it is eliminated because no pigment is used in this process. Reproducibility of color is extremely good because of standardized dyes and standardized colors. Uniformity of fluid concentration is easily maintained even during very long runs as no large amounts of volatile solvents are used which require constant adjustment. Needless to say, these advantages render the present fluid much less costly and especially suitable for modern mass production methods.

The following examples will serve further to illustrate the invention:

EXAMPLE 1

50 parts by weight of urea were dissolved in 450 parts water in a stainless steel tank equipped with an agitator and means for heating. 40 parts by weight of a direct dye, Pontamine Brilliant Green GX, DuPont which is a mechanical mixture of the following two direct dyes: 86% Pontamine Fast Yellow 4GL, C.I. (Color Index) Direct Yellow 44, 14% Pontamine Sky Blue 6BX, C.I. Direct Blue 1, were dissolved in the urea solution, with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation, to a second vessel containing 500 parts by weight of aqueous, cationic polyhydroxypolyalkylenepolyurea-formaldehyde resin solution of the type described in U.S. Pat. 2,699,435 (Uformite 700, Rohm & Haas) having an N.V.S. concentration of approximately 30%. The resulting solution was agitated for 15 minutes and 8.8 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 10 minutes' mixing 1 part by weight of surfactant Igepal CO 630, General Aniline, a 100% active liquid nonionic surfac-

tant, i.e., nonylphenoxypoly(ethylene oxide) was slowly added.

The fluid had the following properties: pH - 7.2, N.V.S. - 29.5%, specific gravity - 1.119 at 77°F., viscosity - 4.03 at 77°F., surface tension - 33.2 dynes/cm 77°F., stability - 68 days.

Just prior to use, 7.5 parts of perfume oil (Bouquet L–P–3580–8, Perry Bros., Inc.) were slowly added with agitation.

The fluid was printed on soft, absorbent 2-ply dry crepe paper, i.e., facial tissue, by commercial direct rotogravure at speeds up to 2900 fpm. The paper was cut and folded into facial tissue form, having an attractive green design imprinted thereon, which print had a color transfer rating of 1 after 4 weeks of aging at room temperature. (The effectiveness of cure by aging is generally measured by water solubility of the resin and determined at room temperature conditions.).

EXAMPLE 2

50 parts by weight of urea were dissolved in 450 parts water in a stainless steel tank equipped with an agitator and means for heating. 13.4 parts by weight of a reactive dye, Cibacron Brilliant Blue BR-P, C.I. Reactive Blue 5, and 6.6 parts by weight of a reactive dye, Cibacron Turquoise Blue G-E, C.I. Reactive Blue 1, Ciba, were dissolved in the urea solution, with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 500 parts by weight of polyhydroxypolyethylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. concentration of approximately 30%. The resulting solution was agitated for 15 minutes and 8.8 parts by weight of 75% Phosphoric Acid catalyst was slowly added. After an additional 10 minutes 1 part by weight of surfactant Igepal CO 630 (General Aniline) was slowly added.

The fluid had the following properties: pH - 6.9, N.V.S. - 29.1%, specific gravity - 1.100, viscosity - 3.98 cps, surface tension - 32.9 dynes/cm., stability - 2 months.

Just prior to use, 7.5 parts of perfume oil (Bouquet L–P–3580–8, Perry Bros., Inc.) were slowly added with agitation.

The fluid was printed on soft, absorbent two-ply dry crepe paper, i.e., toilet tissue, by commercial direct rotogravure at speeds up to 2900 fpm. The paper was cut and rolled into toilet tissue form, having an attractive blue design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging at room temperature.

EXAMPLE 3

50 parts by weight of urea were dissolved in 450 parts water in a stainless steel tank equipped with an agitator and means for heating. 19.4 parts by weight of a reactive dye, Drimarine Scarlet Z-GL P.A.F., C.I. Reactive Red 19, Sandoz, and .6 part by weight of a reactive dye, Drimarine Red Z–2B P.A.F., C.I. Reactive Red 17, Sandoz, were dissolved in the urea solution, with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 500 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. concentration of approximately 30%. The resulting solution was agitated for 15 minutes and 8.8 parts by weight of 75% Phosphoric Acid catalyst was slowly added. After an additional 10 minutes mixing 1 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH - 7.0, N.V.S. - 24.9%, specific gravity - 1.101, viscosity - 3.32 cps, surface tension - 31.8 dynes/cm., stability - 49 days.

Just prior to use, 7.5 parts of perfume oil (Bouquet L–P–3580–8, Perry Bros., Inc.) was slowly added with agitation.

The fluid was printed on soft, absorbent two-ply dry crepe paper, i.e., facial tissue, by commercial direct rotogravure at speeds up to 2900 fpm. The paper was cut and folded into facial tissue form, having an attractive pink design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging at room temperature.

EXAMPLE 4

41.66 parts by weight of urea were dissolved in 291.65 parts water in a stainless steel tank equipped with an agitator and means for heating. 21.99 parts by weight of a direct dye, Pontamine Fast Yellow RL, C.I. Direct Yellow 50, DuPont, and 2.99 parts by weight of a direct dye, Pontamine Fast Brown NP, C.I. Direct Brown 95, DuPont, were dissolved in the urea solution, with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 500 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. concentration of approximately 30%. The resulting solution was agitated for 15 minutes and 8.33 parts by weight of 75% Phosphoric Acid catalyst was slowly added. After an additional 10 minutes' mixing .83 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH - 7.4, N.V.S. - 26.9%, specific gravity - 1.124, viscosity - 5.83 cps, surface tension - 32.8 dynes/cm., stability - 67 days.

Just prior to use 6.25 parts of perfume oil (Bouquet L–P–3580–8, Perry Bros., Inc.) was slowly added with agitation.

The fluid was printed on soft, absorbent two-ply dry crepe paper, i.e., facial tissue, by direct rotogravure at speeds up to 2900 fpm. The paper was cut and rolled into toilet tissue form, having an attractive gold design imprinted thereon, which print had a color transfer rating of 1 after 4 weeks of aging at room temperature.

EXAMPLE 5

In 100 parts water, 6 parts by weight of the direct dye, Pontamine Brilliant Green GX, were dissolved with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts NH_4Cl catalyst were slowly added.

The fluid had the following properties: pH - 6.6, N.V.S. - 17.7%, specific gravity - 1.082, viscosity - 3.05 cps, surface tension - 48.0 dynes/cm., stability - 149 days.

The fluid was printed with a 19 inch wide commercial rotogravure printing unit at speeds up to 3,000 fpm on soft, absorbent two-ply dry crepe tissue, i.e., facial tissue. The paper had an attractive green design imprinted thereon, which print had a color transfer rating of 2 after 4 weeks of aging at room temperature.

EXAMPLE 6

In 100 parts water, 3.88 parts by weight of the reactive dye, Drimarine Scarlet Z-GL P.A.F., C.I. Reactive Red 19, Sandoz, and 0.12 part by weight of the reactive dye, Drimarine Red Z–2B P.A.F., C.I. Reactive Red 17, Sandoz, were dissolved with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts NH_4Cl catalyst were slowly added.

The fluid had the following properties: pH - 6.4, N.V.S. - 18.5%, specific gravity - 1.084, viscosity - 3.74 cps, surface tension - 51.6 dynes/cm., stability - 140 days.

The fluid was printed with a 19 inch wide commercial rotogravure printing unit at speeds up to 3,000 fpm on soft, absorbent two-ply dry crepe tissue, i.e., facial tissue. The paper had an attractive red design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging at room temperature.

EXAMPLE 7

In 100 parts water, 3.33 parts by weight of the reactive dye, Cibacron Brilliant Blue BR, C.I. Reactive Blue 5, Ciba, and 0.67 parts by weight of the reactive dye, Cibacron Turquoise Blue G, C.I. Reactive Blue 7, Ciba, were dissolved with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts of NH_4Cl catalyst was slowly added.

The fluid had the following properties: pH - 6.4, N.V.S. - 17.4%, specific gravity - 1.076, viscosity - 2.83 cps, surface tension - 39.1 dynes/cm., stability - 90 days.

The fluid was printed with a 19 inch wide commercial rotogravure printing unit at speeds up to 3,000 fpm on soft, absorbent two-ply dry crepe tissue, i.e., facial tissue. The paper had an attractive blue design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks aging at room temperature.

EXAMPLE 8

In 100 parts water, 5.0 parts by weight of the direct dye, Pontamine Fast Yellow RL, C.I. Direct Yellow 50, DuPont, and 1 part by weight of the direct dye, Pontamine Fast Brown NP, C.I. Direct Brown 95, DuPont, were dissolved with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts of NH_4Cl catalyst were slowly added.

The fluid had the following properties: pH - 6.7, N.V.S. - 18.6%, specific gravity - 1.087, viscosity - 3.49 cps, surface tension - 47.7 dynes/cm., stability - 92 days.

The fluid was printed with a 19 inch wide commercial rotogravure printing unit at speeds up to 3,000 fpm on soft, absorbent two-ply dry crepe tissue, i.e., facial tissue. The paper had an attractive yellow design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging at room temperature.

EXAMPLE 9

In 100 parts water, 5.88 parts by weight of the acid dye, Lanasy Brilliant Blue GL, C.I. Acid Blue 127, Sandoz, and 0.6 part by weight of the direct dye, Erie Brilliant Violet B Conc. (200%), C.I. Direct Violet 9, Allied Chemical, 0.6 part by weight of the direct dye, Pontamine Black ETP, C.I. Direct Black 38, DuPont, were dissolved with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts of NH_4Cl catalyst was slowly added.

The fluid had the following properties: pH - 6.4, N.V.S. - 19.4%, specific gravity - 1.088, viscosity - 4.67 cps, surface tension - 34.4 dynes/cm., stability - 90 days.

The fluid was printed with a 19 inch wide commercial rotogravure printing unit at speeds up to 3,000 fpm on soft, absorbent two-ply dry crepe tissue, i.e, facial tissue. The paper had an attractive blue design imprinted thereon, which print had a color transfer rating of 2 after 4 weeks of aging.

EXAMPLE 10

In 100 parts water, 4 parts by weight of the direct dye, Pontamine Fast Scarlet 4BA, C.I. Direct Red 24, DuPont, were dissolved with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having and N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts of NH_4Cl catalysts were slowly added.

The fluid had the following properties: pH -6.4, N.V.S. - 18.3%, specific gravity - 1.086, viscosity - 3.90 cps, surface tension - 44.2 dynes/cm., stability - 90 days.

The fluid was printed with a 19 inch wide commercial rotogravure printing unit at speeds up to 3,000 fpm on soft, absorbent two-ply dry crepe tissue, i.e., facial tissue. The paper had an attractive red design imprinted thereon, which print had a color transfer rating of 2 after 4 weeks of aging.

EXAMPLE 11

10 parts by weight of urea were dissolved in 90 parts water. 3 parts by weight of the direct dye, Fiber Black VF, C.I. Direct Black 38, Dupont, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly,

with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2.50 parts of 75% Phosphoric Acid catalyst and 4.0 parts of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.8, stability - 68 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply wet crepe tissue, i.e., napkin base stock. The paper had an attractive black design imprinted thereon, which print had a color transfer rating of 1 after 4 weeks of aging.

EXAMPLE 12

100 parts by weight of urea were dissolved in 400 parts water. 19.4 parts by weight of the reactive dye, Drimarine Scarlet ZGL, C.I. Reactive Red 19, Sandoz, and 0.6 parts by weight of the reactive dye, Drimariune Red Z2B, Sandoz, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 500 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde resin (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 1 hour and 10 parts NH_4Cl catalyst was slowly added. When mixed, 2 parts or surfactant, Pluronic L64, Wyandotte, and 7.5 parts perfume oil (Bouquet L–P–3580–8, Perry Bros, Inc.) were added.

The fluid had the following properties: pH - 6.4, N.V.S. - 27.5%, specific gravity - 1.116, viscosity - 4.83 cps, surface tension - 35.7 dynes/cm., stability - 43 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply dry crepe tissue, i.e., table napkin base stock. The paper was embossed, cut and folded into napkins having an attractive pink design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging.

EXAMPLE 13

100 parts by weight of urea were dissolved in 90 parts water. 3 parts by weight of the direct dye, Solophenyl Turquoise Blue GTL Extra, C.I. Direct Blue 86, Geigy, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas). The resulting solution was agitated for 10 minutes and 2.5 parts 75% Phosphoric Acid catalyst and 0.4 parts of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.5, stability - 68 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply wet crepe tissue, i.e., napkin base stock. The paper had an attractive turquoise design imprinted thereon, which print had a color transfer rating of 1 after 4 weeks of aging.

EXAMPLE 14

10 parts by weight of urea were dissolved in 90 parts water. 2.25 parts by weight of the direct dye, Berkshire Direct Fast Scarlet 4 GS, C.I. Direct Red 24, and 0.75 parts by weight of the direct dye, Berkshire Bond yellow CG, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) with an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts 75% Phosphoric Acid catalyst and 0.4 parts of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.7, stability - 42 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply wet crepe tissue, i.e., napkin base stock. The paper had an attractive reddish-yellow design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging.

EXAMPLE 15

10 parts by weight of urea were dissolved in 90 parts water. 2.25 parts by weight of the direct dye, Diphenyl Golden Yellow RP, Geigy, and 0.75 parts by weight of the direct dye, Diphenyl Brown 3 GT Supra, C.I. Direct Brown 154, Geigy, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts of 75% Phosphoric Acid catalyst and 0.4 parts of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.8, stability - 49 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply wet crepe tissue, i.e., napkin base stock. The paper had an attractive yellowish-brown design imprinted thereon, which print had a color transfer rating of 1 after 4 weeks of aging.

EXAMPLE 16

10 parts by weight of urea were dissolved in 90 parts water. 3 parts by weight of the direct dye, Solophenyl Turquoise Blue GTL Extra, C.I. Direct Blue 86, Geigy, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylene-polyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts of 75% Phosphoric Acid catalyst and 0.4 parts of Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.5, stability - 68 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, one-ply

sized wet crepe tissue, basis weight 20.6 lbs./ream, made on an experimental paper machine. The paper had a turquoise design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging.

EXAMPLE 17

10 parts by weight of urea were dissolved in 90 parts water. 3 parts by weight of the direct dye, Solophenyl Turquoise Blue GTL Extra, C.I. Direct Blue 86, Geigy, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts 75% H_3PO_4 catalyst and 0.4 parts of Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.5, stability - 28 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent one-ply unsized wet crepe tissue, basis weight 20.6 lbs./ream. The paper had an attractive turquoise design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging.

EXAMPLE 18

10 parts by weight of urea were dissolved in 90 parts water. 3 parts by weight of the direct dye, Solophenyl Turquoise Blue GTL Extra, C.I. Direct Blue 86, Geigy, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of 30%. The resulting solution was agitated for 10 minutes and 25 parts of 75% H_3PO_4 catalyst and 0.4 parts by weight of Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.5, stability - 68 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on one-ply bond paper, i.e., basis weight 36.4 lbs./ream. The paper had an attractive turquoise design imprinted thereon, which print had a color transfer rating of 0 after 4 weeks of aging.

EXAMPLE 19

6 parts by weight of urea were dissolved in 94 parts water. 4.0 parts by weight of the direct dye, Durafast Orange 4 GLL, C.I. Direct Orange 72, Berkshire, and 1.0 parts by weight of the direct dye, Pontamine Fast Brown NP, C.I. Direct Brown 95, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. of approximately 30%. The resulting solution was agitated for 10 minutes and 1.76 parts of 75% Phosphoric Acid catalyst and 0.4 parts surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH - 6.75, stability - 29 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply dry crepe tissue, i.e., facial type. The paper had an attractive golden yellow design imprinted thereon, which print had a color transfer rating of 2 after 2 weeks of aging.

EXAMPLE 20

6 parts by weight of urea were dissolved in 94 parts water. 2.8 parts by weight of the direct dye, Solophenyl Turquoise Blue GTL Extra, C.I. Direct Blue 86, Geigy, and 1.2 parts by weight of the direct dye, Direct Brilliant Blue P–5BC, C. I. Direct Blue 25, Ciba, were dissolved in the above solution with agitation and heating to approximately 140°F. The resulting solution was added slowly, with agitation to a second vessel containing 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas). The resulting solution was agitated for 10 minutes and 1.76 parts 75% H_3PO_4 catalyst and 0.2% Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 7.0, stability - 34 days.

The fluid was printed at 300 fpm on a 15 inch wide laboratory rotogravure printing unit on soft, absorbent two-ply dry crepe tissue, i.e., facial tissue. The paper had an attractive blue design imprinted thereon, which print had a color transfer rating of 2 after 4 weeks of aging.

EXAMPLE 21

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 2 parts by weight of a direct dye, Pontamine Fast Yellow RL, C.I. Direct Yellow 50, DuPont, were dissolved in the urea-water solution, with agitation and heated to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 10 minutes' of mixing, 0.4 parts by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 7.5, stability - 117 days.

The fluid was applied by hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The yellow imprinted area had a rating of 1 after 4 weeks of aging.

EXAMPLE 22

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of a direct dye, Pontamine Fast Yellow RL, C.I. Direct Yellow 50, DuPont, and were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts by weight of 75% Phosphoric Acid catalyst

were slowly added. After an additional 10 minutes' of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH 7.5, stability - 117 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The yellow imprinted area had a transfer rating of 2 after 4 weeks of aging.

EXAMPLE 23

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 6 parts by weight of a direct dye, Pontamine Fast yellow RL, C.I. Direct Yellow 50, Du-Pont, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 10 minutes' of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH - 7.6, stability - 110 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The yellow imprinted area had a transfer rating of 3 after 4 weeks of aging.

EXAMPLE 24

2 parts by weight of a direct dye, Pontamine Fast Scarlet 4BA, C.I. Direct Red 24, Dupont, were added to 100 parts of water in a container equipped with an agitator and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 4 parts by weight of ammonium chloride catalyst were slowly added.

The fluid had the following properties: pH - 6.4, stability - 35 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The red imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 25

4 parts by weight of a direct dye, Berkshire Direct Fast Scarlet 4BKA, C.I. Direct Red 24, were added to 100 parts of water in a container equipped with an agitator and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts by weight of NH_4Cl catalyst were slowly added.

The fluid had the following properties: pH - 6.1, stability - 62 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The red imprinted area had a transfer rating of 1 after 4 weeks of aging.

EXAMPLE 26

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of a direct dye, Solophenyl Turquoise Blue GTL, Extra, C.I. Direct Blue 86, Geigy, were dissolved in the ureawater solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 5 minutes of mixing, 0.4 parts by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.8, stability - 47 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The turquoise imprinted area had a transfer rating of 1 after 4 weeks of aging.

EXAMPLE 27

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 6 parts by weight of a direct dye, Solophenyl Turquoise Blue GTL Extra, C.I. Direct Blue 86, Geigy, were dissolved in the aqueous urea solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 5 minutes of mixing, 0.4 parts by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.8, stability - 47 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The turquoise imprinted area had a transfer rating of 2 after 4 weeks of aging.

EXAMPLE 28

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of a direct dye, DuPont Fiber Black VF, C.I. Direct Black 38, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 10 minutes of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 7.6, stability - 77 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The black imprinted area had a transfer rating of 1 after 4 weeks of aging.

EXAMPLE 29

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 3 parts by weight of a direct dye, Golden Yellow RP, Geigy, and 1 part by weight of a direct dye, Pontamine Brown N3G, C.I. Direct Brown 154, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 10 minutes of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH - 7.3, stability - 77 days.

The fluid was applied by a hand operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The brownish-yellow imprinted area has a transfer rating of 3 after 4 weeks of aging.

EXAMPLE 30

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of a reactive dye, Reactone Turquoise Blue FGL, C.I. Reactive Blue 18, Geigy, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 5 minutes of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fluid had the following properties: pH - 7.0, stability - 77 days.

The fluid was applied by a hand operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The turquoise imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 31

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of an acid dye, Brilliant Acid Blue G2L, Geigy, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepoly-urea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.50 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 10 minutes of mixing, 0.4 parts by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.6, stability - 25 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The light blue imprinted area had a transfer rating of 2 after 4 weeks of aging.

EXAMPLE 32

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of a reactive dye, Procion yellow 4RD, I.C.I., were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.50 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an addition 5 minutes of mixing, 0.4 parts by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.6, stability - 75 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The yellow imprinted area had a transfer rating of 3 after 4 weeks of aging.

EXAMPLE 33

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of an acid dye, Metanil Yellow P Conc., C. I. Acid Yellow 36, Allied Chemical, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.5 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 5 minutes of mixing, 0.4 parts by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 6.8, stability - 20 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The yellow imprinted area had a transfer rating of 3 after 4 weeks of aging.

EXAMPLE 34

3.92 parts by weight of an acid dye, Lanasyn Brilliant Blue GL, C.I. Aicd Blue 127, Sandoz, and 0.08 parts by weight of a direct dye, Erie Brilliant Violet B Conc. (200%), C.I. Direct Violet 9, Allied Chemical, and 0.08 part by weight of a direct dye, Pontamine Black ETP, C.I Direct Black 38, were dissolved in water, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting

solution was agitated for 10 minutes and 4 parts by weight of Ammonium Chloride catalyst were slowly added.

The fluid had the following properties: pH - 5.5, viscosity - 3.70 cps, stability - 15 days.

The fluid was applied by hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The blue imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 35

10 parts by weight of urea were added to 90 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of a reactive dye, Primazin Green GL, BASF, were dissolved in the urea-water solution, with agitation and heating to 100°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 2.50 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 5 minutes of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was slowly added.

The fliud had the following properties: pH - 6.7, stability - 37 days, gel.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The green imprinted area had a transfer rating of 2 after 4 weeks of aging.

EXAMPLE 36

6 parts by weight of urea were added to 94 parts of water in a container equipped with an agitator and means for heating. 4 parts by weight of an acid dye, Berkshire Phloxine G. Conc. (150%), C.I. Acid Red 1, were dissolved in the urea-water solution, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 5 minutes and 1.76 parts by weight of 75% Phosphoric Acid catalyst were slowly added. After an additional 5 minutes of mixing, 0.4 part by weight of surfactant Igepal CO 630, General Aniline, were slowly added.

The fluid had the following properties: pH - 7.1, stability - 21 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The red imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 37

3.08 parts by weight of a reactive dye, Cibacron Yellow G, C.I. Reactive Yellow 6, Ciba, and 0.88 part by weight of a reactive dye, Cibacron Blue 3G, C.I. Reactive Blue 2, and 0.04 part of a reactive dye, Cibacron Turquoise Blue GF, C.I. Reactive Blue 15, were dissolved in 100 parts by weight of water, with agitation and heating to 140°F. The resulting solution was added slowly with agitation to 100 parts by weight of polyhydroxypolyalkylenepolyureaformaldehyde condensate (Uformite 700, Rohm & Haas) having an N.V.S. content of approximately 30%. The resulting solution was agitated for 10 minutes and 4 parts by weight of Ammonium Chloride catalyst were slowly added.

The fluid had the following properties: pH - 5.4, viscosity - 3.37 cps, stability - 32 days.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply dry crepe paper, i.e., facial tissue. The green imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 38

100 parts by weight of resin polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) 30% N.V.S., were modified by addition of 90 parts by weight of water, 30 parts by weight of urea, 1.76 parts by weight of 75% Phosphoric Acid and mixed unitl solution was homogeneous.

3.88 parts by weight of a reactive dye, Drimarine Scarlet Z-GL P.A.F., C.I. Reactive Red 19, Sandoz, 0.12 part by weight of a reactive dye, Drimarine Red Z-2B P.A.F., C.I. Reactive Red 17, Sandoz, were added directly to the modified resin solution described above with agitation and heating to 130°F. The dye-resin was mixed until solution was complete. Then 0.4 parts by weight of surfactant Igepal CO 630, General Aniline was added, slowly.

The fluid had the following properties: pH - 6.8, N.V.S. - 22.7%, specific gravity - 1.102, viscosity - 3.69 cps, surface tension - 33.3 dynes/cm.

The fluid was applied by a hand-operated simulated rotogravure method on soft-absorbent two-ply crepe paper, i.e., facial tissue. The pink imprinted area had a transfer rating of 1 after 4 weeks of aging.

EXAMPLE 39

100 parts by weight of resin polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) 30% N.V.S. were modified by addition of 90.0 parts by weight of water, 10 parts by weight of urea and mixed until solution was homogeneous.

4 parts by weight of a direct dye, Pontamine Fast Yellow RL, C.I. Direct yellow 50, DuPont, were added directly to the modified resin solution described above with agitation and heating to 140°F. The dye-resin was mixed until solution was complete. Then 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was added, slowly.

The fluid had the following properties: pH - 6.75, N.V.S. - 23.2%, specific gravity - 1.106, viscosity - 3.55 cps, surface tension - 32.9 dynes/cm.

The fluid was applied by hand-operated simulated rotogravure method on soft, absorbent two-ply crepe paper, i.e., facial tissue. The yellow imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 40

100 parts by weight of resin polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) 30% N.V.S., were modified by addition of 90 parts by weight of water, 30 parts by weight of urea, 1.76 parts by weight of 75% Phosphoric Acid and mixed until the solution was homogeneous.

4 parts by weight of an acid dye, Brilliant Acid Blue G2L, Geigy, were added directly to the modified resin solution described above with agitation and heating to 140°F. The dye-resin was mixed until solution was com-

plete. Then 0.4 part by weight of surfactant Igepal CO 630, General Aniline, was added, slowly.

The fluid had the following properties: pH - 7.0, N.V.S. - 23.2%, specific gravity-1.100, viscosity - 4.08 cps, surface tension - 33.0 dynes/cm.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply crepe paper, i.e., facial tissue. The blue imprinted area had a transfer rating of 0 after 4 weeks of aging.

EXAMPLE 41

100 parts by weight of resin polyhydroxypolyalkylenepolyurea-formaldehyde condensate (Uformite 700, Rohm & Haas) 30% N.V.S., were modified by addition of 90 parts by weight of water, 10 parts by weight of urea and 25 parts by weight of 75% Phosphoric Acid and mixed until solution was homogeneous.

6 parts by weight of a direct dye, Pontamine Fast Yellow RL, C.I. Direct Yellow 50, DuPont, were added directly to the modified resin solution described above with agitation and heating to 140°F. The dye-resin was mixed until solution was complete. Then 0.4 part by weight of surfactant Igepal CO 630, General Aniline, were added, slowly.

The fluid had the following properties: pH - 6.85, N.V.S. - 23.8%, specific gravity - 1.108, viscosity - 4.04 cps, surface tension - 33.3 dynes/cm.

The fluid was applied by a hand-operated simulated rotogravure method on soft, absorbent two-ply crepe paper, i.e., facial tissue. The yellow imprinted area had a transfer rating of 1 after 4 weeks of aging.

What is claimed is:

1. A low-viscosity printing fluid suitable for printing cellulose webs which comprises an aqueous solution of a watersoluble, cationic, thermosetting, polyhydroxypolyalkylenepolyurea-formaldehyde resin condensate and a water-soluble dye compatible with said resin, said dye and resin mixture having a stability of from about 1 hour to in excess of 4 months and a transference value of from about 0 to about 4, and a viscosity of less than 20 cps at 77°F.

2. A low-viscosity printing fluid as claimed in claim **1** wherein the resin is a water-soluble, cationic, thermosetting polyhydroxypolyalkylenepolyurea-formaldehyde resin condensate prepared by a process which comprises reacting between about 0° and 100°C., in the presence of water, epichlorophydrin and an alkylene polyamine having two to three carbon atoms in the alkylene portion thereof in a mole ratio from 1:1 to 1.4:1 until an aqueous solution of the resulting polyhydroxypolyalkylenepolyamine at a concentration of about 46% has a viscosity from J to Z, at 25°C. on the Gardner-Holdt scale; reacting said polyhydroxypolyalkylenepolyamine with urea between 100° and 200°C. in a ratio from 0.5:1 to 1.8:1 of urea per —NH—group of said polyhydroxypolyalkylenepolyamine until an aqueous 45% solution of the resulting polyhydroxypolyalkylenepolyurea has a viscosity from B to Z_3 at 25°C. on the Gardner-Holdt scale; and reacting said polyhydroxypolyalkylenepolyurea with formaldehyde in a solution at a pH between 7 and 9.5.

3. A low-viscosity printing fluid as claimed in claim **2** which is free from tinctorial particulate matter and which has a viscosity of less than 15 cps at 77°F., a stability of from about 1 hour to in excess of 4 months, and a transference value of from about 0 to about 4 as measured against standardized solutions of a standard thermosetting resin and a standard dye.

4. A low-viscosity printing fluid as claimed in claim **3** which has a transference value of from 0 to 2.

5. A low-viscosity printing fluid as claimed in claim **1** wherein the resin is a water-soluble, cationic, thermosetting polyhydroxypolyalkylenepolyurea-formaldehyde resin condensate prepared by a process which comprises reacting between about 0° and 100°C., in the presence of an inert volatile solvent, epichlorohydrin and an alkylene polyamine having two to three carbon atoms in the alkylene portion thereof in a mole ratio of 1:1 to 1.4:1 yielding soluble reaction products, continuing this reaction until an aqueous solution of the resulting polyhydroxypolyalkylenepolyamine hydrochloride at a polyamine concentration of about 46% has a viscosity of J to Z_7 at 25°C. on the Gardner-Holdt scale, neutralizing the hydrochloride portion thereof, reacting the polyhydroxypolyalkylenepolyamine with urea between 100° and 200°C. with evolution of ammonia, the ratio of moles of urea per —NH— group of said polyhydroxypolyalkylenepolyamine being from 0.5:1 to 1.8:1, continuing this reaction until an aqueous 45% solution of the resulting polyhydroxypolyalkylenepolyurea has a Gardner-Holdt viscosity at 25°C. of B to Z_3, and reacting said polyhydroxypolyalkylenepolyurea with 0.5 to 3 moles of formaldehyde per —NH— group of said polyhydroxypolyalkylenepolyurea.

6. A low-viscosity printing fluid as claimed in claim **4** which is free from pigmented particulate matter and which has a viscosity of less than 15 cps at 77°F., a stability of from about one week to in excess of four months, and a transference value of from about 0 to about 3 as measured against standardized solutions of a standard thermosetting resin and a standard dye.

7. A low-viscosity printing fluid as claimed in claim **1** wherein the resin is a water-soluble, cationic, thermosetting polyhydroxypolyalkylenepolyurea-formaldehyde resin condensate prepared by a process which comprises reacting between about 0° and 100°C. in the presence of water epichlorohydrin and a polyethylenepolyamine in a mole ratio from 1:1 to 1.4:1 yielding soluble polyhydroxypolyalkylenepolyamines, continuing this reaction until an aqueous solution of the resulting polyhydroxypolyalkylenepolyamine hydrochloride at a polyamine content of about 46% has a viscosity from T to Z_4 at 25°C. on the Gardner-Holdt scale, neutralizing the hydrochloride portion thereof, reacting the polyhydroxypolyalkylenepolyamine with urea between 100° and 200°C. with evolution of ammonia until an aqueous solution containing about 45% of the resulting polyhydroxypolyalkylenepolyurea has a Gardner-Holdt viscosity at 25°C. of F to Z, the ratio of urea to —NH— group of said polyhydroxypolyalkylenepolyamine in the reaction mixture being between 0.5:1 and 1.8:1, and reacting in aqueous solution at a pH between 7 and 9.5 formaldehyde and said polyhydroxypolyalkylenepolyurea in a ratio of 1 to 2 moles of formaldehyde per —NH— group of said polyurea.

8. A low-viscosity printing fluid as claimed in claim **7** which is substantially free from volatile solvents having a vapor pressure less than that of water and which has a stability of from about one week to in excess of four months, a transference value of from about 0 to about 2 as measured against standardized solutions of a standard thermosetting resin and a standard dye, a viscosity in the range of from about 3.0 cps to about 7.0 cps, and a surface tension of from about 30 dynes/cm. to about 60 dynes per centimeter.

9. A fibrous web product having a permanent print thereon which is derived from a fluid as claimed in claim **1.**

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