

1

2,936,241

## NON-PRINTING INDICIA INK

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No Drawing. Application May 16, 1957  
Serial No. 659,484

3 Claims. (Cl. 106—25)

The invention relates to inks. More particularly, it relates to an ink which is suitable for use as a non-printing indicia medium on offset printing plates of the colloid type.

On such type printing plates, there is usually present a coating characterized by an inherently water-swallowable nature, this characteristic being employed to repel greasy lithographic printing ink, thus enabling the coatings to constitute the non-printing portions of lithographic offset printing plates. Upon these coatings, it is customary to apply relatively hard grease receptive images which are inked to form printing portions of the plates.

In lithographic printing, two immiscible substances are constantly being brought together at the surface of the lithographic plate. Since it is necessary on the one hand to maintain, at the image portions, a relatively heavy unemulsified ink body, and on the other hand, to replenish continually the water in the non-printing portions of the plate to replace that carried away as the plate makes an impression, the operating range is relatively narrow. Maintaining this operating range is in a good part dependent upon the use of an acid in the water furnished to the non-printing portions. The effect of the acid is to prevent emulsification of greasy ink and to aid in keeping tiny particles of greasy ink from becoming attached to the non-printing portions. Such acid may be furnished either directly from within a colloidal printing plate body, externally from a fountain solution roller or both. In the latter situation, the two sources of acidity supplement one another to control the ink handling function.

In U.S. Patent 2,532,866 to Toland et al., issued December 5, 1950, there are disclosed examples of colloid coatings for offset printing wherein there are included polyvinyl alcohol or gelatin as the colloid material and a water soluble dibasic acid such as oxalic, tartaric, succinic, or fumaric acid. In U.S. Patent 2,532,865 to Toland et al., issued December 5, 1950, there is disclosed a colloid coating including polyvinyl alcohol, oxalic acid and a melamine-formaldehyde resin. The resin, in the presence of the oxalic acid, is cured to form hard water-impervious masses distributed throughout the coating and especially at its surface. The coating thus presents, on the one hand, a multiplicity of highly grease-retentive anchor points to which a greasy typewritten image or character may be very firmly attached; and on the other hand, tiny intermediate areas of water swollen colloid, which if first moistened, will hold water and repel greasy ink subsequently applied against the surface of the plate.

In utilizing an offset printing plate having a coating such as disclosed in the Toland et al. patents referred to above, it has been found that known nonprinting indicia inks cause the plate in the area of the indicia markings to become sensitive to the hydrophobic press ink resulting in the reproduction of the indicia markings on the print. It is believed that such sensitivity may be due to two factors. One factor is the excess curing or cross-linking of the polyvinyl alcohol due to the residual acid in the

2

plate whereby its swellable property is appreciably reduced with a consequent loss of ink rejecting power. The second factor is the interaction between the residual acid in the plate and the components of the indicia ink.

Accordingly, it is the primary object of the present invention to provide an improved non-printing ink for use as an indicia medium on offset printing plates of the colloid type.

It is further intended to provide a non-printing ink for use as an indicia medium on offset printing plates of the colloid type which preserves the hydrophilic nature of the plate in the area of indicia printing thereby eliminating the tendency of the plate to become sensitive to hydrophobic press ink in such area.

In accordance with the invention, there is provided a non-printing ink for use with an offset printing plate of the colloid type comprising a hydrophilic plasticizer, a relatively cohesive film former, a coloring agent selected from the group consisting of inorganic pigments and water soluble organic dyes and a relatively mild base which is substantially insoluble in neutral and alkaline medium.

For a better understanding of the present invention, together with other and further objects thereof, reference is had to the following description and its scope will be pointed out in the appended claims.

In utilizing colloid type offset plates, as explained hereinabove, the polyvinyl alcohol water swellable colloid may be modified by adding melamine formaldehyde resin and a dibasic acid thereto, both of these materials being dispersed throughout the coating. The resin, in the presence of this acidic material, is cured to form hard water-impervious masses distributed throughout the coating and especially at its surface. The coating thus presents both a multiplicity of highly grease-retentive anchor points to which a greasy typewritten image or character may be firmly attached and tiny intermediate areas of water swollen colloid which, if first moistened, will hold water and repel greasy ink subsequently applied against the surface of the plate.

In such coating, it is believed that the polyvinyl alcohol is probably undergoing continuous curing due to the presence of unreacted melamine-formaldehyde resin and free dibasic acid in the plate. However, there is a tendency for the curing to reach a stable point and the balance of the distribution of grease repellent and grease receptive areas in the plate is advantageously maintained. Actually, the acid may even in time tend to disappear. However, when indicia ink is added, this balance is upset in the plate and the curing of the polyvinyl alcohol tends to proceed further, i.e., further cross-linking of the polyvinyl alcohol occurs with the result that some of the grease repellent areas become sensitive to hydrophobic press ink. In addition, another undesired phenomenon is the interaction of the residual free acid in the plate and the components of the ink (particularly in the case in which the color is a spirit-soluble dye, which has an inherently greasy nature.)

Accordingly, the salient point of the invention is the incorporation into the non-printing ink of an alkaline component, which is normally substantially insoluble in neutral and alkaline medium. This alkaline component, which may suitably be a salt consisting of a relatively electropositive metal radical such as the alkaline earth metals and a weak acid radical such as the carbonate, phosphate, oxalate, tartrate, etc. ions, reverses the curing action, i.e., the hardening cross-linking action when the ink is applied to the plate by removing both the residual acid and by breaking up some of the cross-linking present by causing some hydrolysis of the polyvinyl alcohol. In this manner, the tendency of the polyvinyl alcohol colloid to become sensitive to hydrophobic press ink in

3

the area of indicia ink is eliminated by preventing excessive curing or cross-linking of the polyvinyl alcohol. Stating it in another manner, the hydrophilic, non-sensitive plate in the area of indicia printing is preserved by the alkaline component due to a conditioned hydrolysis of the polyvinyl alcohol surface, and the possibility for interaction between the residual acid in the plate and the components of the ink is substantially eliminated.

The plasticizer required is a hydrophilic material which is relatively non-volatile and which maintains a good water balance between the atmosphere and the plate. Suitable materials for use as the plasticizer are polyhydric alcohols such as glycerine, diethylene glycol, polyethylene glycols 200 through 600 and polypropylene glycol 400.

The binder should be a cohesive film former that keeps the ink in place thereby preventing smudging, and a material that wets readily. Examples of suitable film formers are dextrin, gum arabic, carboxymethyl cellulose and polyvinyl alcohol.

The coloring agent may be an inorganic pigment or a water soluble dye. Although some spirit soluble dyes may be used, they present the disadvantage of being grease receptive. An example of a suitable inorganic material is Ultramarine Blue which has an attractive blue color, is nonreactive, and is hydrophilic. Suitable organic dyes, of course, are sulfonated dyes which are water but not spirit soluble.

The filler should be a powdery insoluble material which lends consistency, texture and workability to the ink. It is not necessary that the filler have "hiding power," that is, ability to diminish the intensity of color of the ink, but it is preferred that it be white or of light color. Examples of suitable fillers are kaolins such as china clay, attapulgite, fuller's earth, and barium sulfate.

The whitening agent is primarily a material which does have good "hiding power." In addition, it should have good flow properties and impart a uniform viscosity and an even spreadability to the ink. Suitable examples of whitening agents are titanium dioxide and zinc oxide.

The base, which is insoluble in alkaline medium, should be a relatively mild one, i.e., one which will provide a pH of from 8 to 9 in the final composition. Suitable examples of such bases are carbonates, phosphates, oxalates, tartrates, etc. of the alkaline earth metals and some magnesium salts of these acids.

The ranges of concentrations of the different constituents in the ink composition, while not critical, should be chosen to provide an advantageous ink. The following ranges have been found to be suitable for a particular embodiment in accordance with the invention.

	Percent
Glycerine .....	25-55
Dextrin .....	10-20
Titanium dioxide .....	0-15
Ultramarine Blue .....	10-30
Calcium carbonate .....	5-25
China clay .....	0-20

The preparation of the ink compositions of the present invention may be performed at room temperatures. A preferable method of preparation is to add the ingredients to the glycerine, stir the resulting slurry vigorously or with a mechanical stirrer and then run the stirred mixture through a colloid dispersion mill until the desired consistency is attained.

The following examples illustrate preferred embodiments of the invention.

#### Example I

An ink was prepared in accordance with the above method containing 29 parts by weight of glycerine, 5 parts by weight of dextrin, 5 parts by weight of Ultramarine Blue and 11 parts by weight of calcium carbonate. This ink had a pH of between 8 and 9 and when used as an

4

indicia medium on colloid-type offset printing plates did not print out at all in a run of 1,000 copies.

#### Example II

The same mixture as that in Example I was made except that there was further added thereto 5 parts by weight of titanium dioxide. The same beneficial results were obtained except that the indicia markings were of a much lighter blue color.

#### Example III

An ink was made, as in the preceding examples, comprising 40 parts by weight of glycerine, 10 parts by weight of dextrin, 5 parts by weight of titanium dioxide, 20 parts by weight of Ultramarine Blue, 10 parts by weight of calcium carbonate and 20 parts by weight of china clay. This ink was a little thicker than those of Examples I and II, but otherwise displayed the same advantageous properties.

#### Example IV

An ink was made as described comprising 40 parts by weight of glycerine, 5 parts by weight of Ultramarine Blue, 10 parts by weight of calcium carbonate, and 15 parts by weight of china clay. This was an effective non-printing indicia ink with a relatively strong blue color.

#### Example V

A non-printing indicia ink was made which comprised 40 parts by weight of glycerine, 5 parts by weight of dextrin, 5 parts by weight of titanium dioxide, 20 parts by weight of Ultramarine Blue, 5 parts by weight of calcium carbonate, and 30 parts by weight of china clay. This was the most viscous ink of all the examples shown, but was workable and had the required properties.

While there have been described what are at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications may be made therein without departing from the invention, and it is, therefore, aimed to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. For use with an offset printing plate, an anhydrous nonprinting indicia ink consisting essentially of the following proportions of ingredients by weights:

	Percent
Glycerine .....	25-35
Dextrin .....	10-20
Titanium dioxide .....	0-15
Ultramarine Blue .....	10-30
Calcium carbonate .....	5-25
China clay .....	0-20

2. For use with an offset printing plate of the colloid type, an anhydrous non-printing indicia ink consisting essentially of a hydrophilic plasticizer selected from the group consisting of glycerine, diethylene glycols, polyethylene glycols, and a polypropylene glycol, a film former selected from the group consisting of dextrin, gum arabic, carboxymethyl cellulose and polyvinyl alcohol, a coloring agent selected from the group consisting of inorganic pigments and water-soluble organic dyes, a weak acid salt having an alkaline component which is normally substantially insoluble in neutral and alkaline media having anions selected from the group consisting of carbonate, phosphate, oxalate and tartrate, a filler, and a whitening agent selected from the group consisting of titanium dioxide and zinc oxide, having the following proportions by weight:

	Percent
Plasticizer .....	25-55
Film former .....	10-20
Filler .....	0-15
Coloring agent .....	10-30
Acid salt .....	5-25

5

3. In combination an offset printing plate of the colloid type having a polyvinyl alcohol water-soluble colloid with a resin and a dibasic acid dispersed therethrough, non-printing indicia former on said plate, said non-printing indicia being formed of an anhydrous hydrophilic ink consisting essentially of the following proportions of ingredients by weights:

	Percent		
Glycerine -----	25-55		1,406,837
Dextrin -----	10-20	10	1,633,500
Titanium dioxide -----	0-15		1,804,245
Ultramarine Blue -----	10-30		1,935,629
Calcium carbonate -----	5-25		2,090,704
China clay -----	0-20		2,186,945
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