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PRINTING INKS

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The present invention relates to printing inks, and relates more particularly to offset metal decorating inks.

At the present time, a greater amount by far of the coloration and decoration of tinplate and of metal sheets is performed by offset printing than by any other method. This method of printing is similar to lithographic printing in that it is based upon the mutual repellency of water and grease.

In the offset method of printing, a plate cylinder which carries the design which is to be imprinted is firstly dampened with water, or with a weak aqueous acid solution as by means of a suitable dampening roller and is then inked by means of an inking roller with an ink having greasy or water-repellent characteristics. The surface characteristics of the plate cylinder are such, due to suitable prior treatment of the printing plate carried thereon, that the non-printing portions thereof retain a sufficient amount of the dampening water or acid solution to repel the ink carried by the inking roller and thus prevent those portions of the printing plate from retaining any ink. The design which is carried by the printing plate is of such character that it repels water but is receptive of an ink having greasy characteristics. Thus when the plate cylinder passes through the dampening and inking phases, the design areas of the printing plate repel the dampening water but retain the ink so that only that portion of the surface of the printing plate or plate cylinder which constitutes the design to be imprinted carries a film of printing ink thereon. In the actual printing operation the ink film which is carried by the plate cylinder is "offset" on to a rubber blanket cylinder which rotates in contact with the plate cylinder. The design which has thus been "offset" upon the blanket cylinder is subsequently transferred to the sheet material which is to be imprinted by passing the sheet material between the blanket cylinder and an impression cylinder which normally presses against the blanket cylinder.

To meet the requirements of the offset printing process, a printing ink must have certain definite characteristics. For example, the ink should be capable of repelling water and should have no tendency to emulsify on the printing press. The ink should also be substantially free of volatile ingredients which might effect premature drying of the ink film upon the printing plate or upon the blanket cylinder. The ink should also have sufficient tack to permit proper transfer of the ink film from the blanket cylinder to the sheet material which is to be imprinted, but should not be so tacky as to destroy the ink design as it is being transferred.

In the decoration of tinplate or metal sheets it is essential that an ink film be obtained upon these materials which is completely dry and which is sufficiently hard and durable to withstand the stresses which are usually applied to such materials in the fabrication of metal products such as cans, bottle caps, etc. Therefore, immediately after printing the metal sheets are subjected to a baking operation which dries the imprinted ink to

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a hard, tough film and which improves the adherence of the dried ink film to the metal. Such baking operations are normally carried out at temperatures of between approximately 250°–325° F. for periods of approximately 10 to 20 minutes, although higher temperatures may also be employed. Therefore, where a printing ink is to be used in the decoration of tinplate or of metal sheets, such printing ink should be capable of withstanding the high baking temperatures normally employed to dry the imprinted ink films without undergoing any substantial change in the color shade of the said ink films.

However, one of the most serious problems in the field of offset metal decorating inks and one of the most difficult to contend with has been the problem of color retention in the imprinted ink film at elevated baking temperatures, particularly where white inks are concerned. For example, the white inks, when subjected to the baking schedules normally utilized to dry the imprinted inks, invariably take on a slight yellow tinge which is highly undesirable in the finished product. Since the pigments customarily employed in printing inks which are to be used in metal decorating operations are those which are normally heat resistant, that is, pigments which are resistant towards decomposition or color change at the temperatures required to dry and to set the imprinted ink films in metal decorating operations, the color change which occurs at baking temperatures is apparently due to a change which occurs in the ink vehicle under these conditions. Such color change upon baking of the imprinted ink film is apparently characteristic of all of the orthodox constructions of metal decorating inks. For example, printing inks employing lithographic varnishes as the vehicle, or which contain substantial amounts of drying oils, or drying oil modified or drying oil fatty acid modified resins all display a tendency to yellow upon baking at the temperatures required to produce a hard, durable film upon metal. Such systems also provide films of limited chemical resistance due to the presence of ester linkages such as occur in drying oils, oleoresinous varnishes, and in alkyd resins. Phenol-formaldehyde resin base vehicles are also notorious for their yellowing tendencies under high bake conditions and are, therefore, of use only in such applications where the yellowing of the baked film is not noticeable. Where white metal decorating inks are concerned, it has been the usual practice in the art to incorporate a certain amount of blue pigment or toner in such inks in an attempt to minimize the effect of the color change which occurs in the imprinted ink film upon baking.

By the present invention, however, there are provided printing inks which have excellent workability on offset printing presses, which form extremely hard and durable films on metal, and which exhibit no color change in the imprinted ink film when such films are subjected to the baking temperatures customarily employed in metal decorating operations. In particular, there is provided a white offset metal decorating ink which displays no yellowing at elevated temperatures and which requires no toning in order to preserve the color shade of the ink.

The printing inks of the present invention consist of pigment coloring material dispersed in a vehicle which consists essentially of a resinous reaction product of epichlorhydrin and bis phenol which acts as the pigment binder material, and a liquid chlorinated biphenyl which constitutes the liquid carrier medium of the inks.

The resin which is utilized as the pigment binder of the inks of the present invention is, as has been mentioned, a resinous reaction product of epichlorhydrin and bis phenol. This is a non-oxidizing linear condensation polymer which exhibits excellent properties of adhesion, flexibility and chemical resistance.

The chlorinated biphenyls which constitute the liquid

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carrier medium of the inks of the present invention are substantially colorless mobile oils. These materials are not ordinarily classified as solvents and, depending upon the degree to which polymerization of the chlorinated biphenyls is carried out, may be either liquid, crystalline, or hard and brittle resinous materials. The chlorinated biphenyls which have been found to be most suited for use in the printing inks of the present invention are the liquid materials having a distillation range within the range of approximately 275°–360° C.

As coloring material for the printing inks herein described, there may be utilized any of the well known heat-resistant insoluble pigment materials such as, for example, ultramarine blue, milori blue, chrome yellow, cadmium yellow, cadmium red, carbon black, etc. To obtain a white metal decorating ink which, after baking, will retain the purity and color shade of the original ink, the use of titanium dioxide as the pigment coloring material is preferred.

Preparation of the printing inks is a comparatively simple process. The vehicle is prepared by heating the resin and the chlorinated biphenyl together at a temperature of approximately 250° F. until a homogeneous blend of the said materials is secured. The pigment may then be dispersed in the vehicle and the finished ink obtained by utilization of the well known 3-roll mill. Since the character of the offset printing process generally requires the use of printing inks having a rather high pigment concentration, it is desirable that the materials forming the vehicle be utilized in such proportion to each other as to provide a relatively fluid blend thereof. Depending upon the properties desired in the finished ink, the resinous binder and the chlorinated biphenyl may satisfactorily be utilized in the proportions to each other of approximately 35% to 65% by weight of the resin to approximately 65%–35% by weight of chlorinated biphenyl.

The following examples are illustrative of the metal decorating inks of the present invention.

Example 1

	Parts by wt.
Titanium dioxide.....	54.0
Resinous reaction product of epichlorhydrin and bis phenol.....	26.5
Chlorinated biphenyl (distillation range 290°–325° C.).....	19.5
	100.0

A metal sheet imprinted with the ink of Example 1 was subjected to four separate successive bakings of 10 minutes each at temperatures ranging from 310° F. to 360° F. without any noticeable change in the color of the imprinted ink film.

The proportions of the materials utilized in preparing the printing inks may be varied as desired depending upon the consistency which it is desired to obtain in the finished ink. Thus, if a heavier bodied ink is desired, the ratio of pigment to vehicle is increased; and where a softer bodied ink is wanted the ratio of pigment to vehicle is decreased. For white printing inks employing titanium dioxide as the pigment coloring material, completely satisfactory results are obtained with inks containing a pigment concentration of approximately 44% to 64% by weight based on the weight of the ink. Different pigments will, of course, necessitate the use of

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different pigment concentrations in the inks of the present invention. However, anyone who is at all familiar with ink formation will have no trouble in determining the necessary amounts of pigment to be utilized in preparing good commercial metal decorating inks, particularly with the following illustrative ink examples as guides.

Example 2

	Parts by wt.
10 Resinous reaction product of epichlorhydrin and bis phenol.....	38.6
Chlorinated biphenyl (distillation range 325° C.–360° C.).....	38.0
Carbon black.....	16.7
15 Milori blue.....	6.7
	100.0

Example 3

20 Resinous reaction product of epichlorhydrin and bis phenol.....	12.2
Chlorinated biphenyl (distillation range 275° C.–320° C.).....	7.8
25 Cadmium yellow.....	80.0
	100.0

Example 4

Resinous reaction product of epichlorhydrin and bis phenol.....	20.5
30 Chlorinated biphenyl (distillation range 290° C.–325° C.).....	13.0
Ultramarine blue.....	66.5
	100.0

While the products herein described constitute preferred embodiments of the present invention, changes may be made therein without departing from the scope of the invention as defined in the appended claims.

40 What is claimed is:

1. A printing ink consisting of a pigment dispersed in a vehicle consisting of approximately 35% to 65% by weight of a resinous reaction product of epichlorhydrin and bis phenol, and approximately 65% to 35% by weight of a liquid chlorinated biphenyl having a distillation range within the range of approximately 275° C. to 360° C.

2. A printing ink consisting of approximately 44% to 64% by weight of titanium dioxide dispersed in approximately 56% to 36% by weight of a vehicle consisting of a fluid blend of a resinous reaction product of epichlorhydrin and bis phenol, and a liquid chlorinated biphenyl having a distillation range within the range of approximately 275° C. to 360° C.

3. A printing ink consisting of approximately 44% to 64% by weight of titanium dioxide dispersed in approximately 56% to 36% by weight of a vehicle consisting of approximately 35% to 65% by weight of a resinous reaction product of epichlorhydrin and bis phenol, and approximately 65% to 35% by weight of a liquid chlorinated biphenyl having a distillation range within the range of approximately 275° C. to 360° C.

References Cited in the file of this patent

65 Epon Resins, Paint, Oil and Chemical Review, vol. 113, No. 23, Nov. 9, 1950, pages 15–18, 48 and 49.