United States Patent Office 3,015,632 Patented Jan. 2, 1962

3,015,632

ELECTRICALLY CONDUCTIVE PRINTING INK AND METHOD OF PRODUCING SAME

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No Drawing. Filed Dec. 31, 1956, Ser. No. 631,458
8 Claims. (Cl. 252—511)

This invention relates to printing ink for use in high-speed printing, either by direct or offset methods, and to a method or methods of producing such ink. Although especially suited for overcoming certain problems connected with the printing of newspapers, it is also well suited for other types of printing where problems similar to those in newspaper printing are present.

Since this invention is primarily concerned with the printing of newspapers, it will be described basically in this connection, and in relation to the special problems involved therein, although it will be understood that the description is also applicable, at least in part, to other kinds of printing.

In the printing of newspapers, electrical charges generated by friction and the negative charge naturally carried by the newsprint and the ink create certain problems, hereinafter set forth in greater detail, and prior attempts to solve these problems have not been successful.

It is a known fact that cellulose and wood fibers from which newsprint and other types of papers are composed possess a strong negative electrical charge which the finished product naturally assumes. Also, during the production of the paper at the mill, and in its high speed travel through printing presses, static electricity is developed as a result of friction between the paper and the machinery through which it passes. This results in the paper developing an even stronger negative charge than it would normally have due to the charge of its elements.

The inks commonly used in printing also possess a negative electrical charge, which is increased in potential due to generation of static electricity as the ink is conducted through the inking system to the paper by means of rollers. As a result, since bodies carrying like charges of electricity tend to repel one another, the transfer of ink to the paper is often poor, resulting in imperfections such as those commonly referred to as "mottling" and "smearing."

The "misting" of ink, which is caused by film splitting when the pigment therein separates from the vehicle, is another problem resulting in part from the static electrical charge generated by the friction between inking rollers and from the negative polarity of inks commonly used in newspaper printing. Since the rollers now used are dielectric, the electrical charge created by the friction between them cannot be dissipated; thus, when two rollers, both of which are negatively charged, contact one another, the electrical charge of each attempts to pass to the other, and as a result electrical arcing could occur which might rupture the ink filament and cause misting.

Another common cause of rupture of the elastic filament of the ink vehicle and consequent misting of the inks now in use is the "milling" of the vehicle and pigment together during the transfer of the ink from one roller to another. The action of the inking rollers as they transfer the ink from the reservoir or fountain is similar to the action of an ink mill. The ink as it is transferred from the fountain or reservoir by the rollers is milled by the action of the rollers. The action of the pigment and the vehicle being milled together during ink transfer, results in the rupture of the elastic filament of the ink vehicle due, at least in part, to the electrical charges generated by the friction between the ink and rollers. When the elastic filament of the ink vehicle is

ruptured, the pigment is separated from the vehicle and misting may result.

Still another factor contributing to the misting of inks is the polarity of the electrical charge naturally carried by the constituents of ordinary printing inks. Since the vehicles commonly employed in ink formulations are negatively charged dielectrics and the carbon black normally used in printing inks is negatively charged, the carbon tends to separate from the vehicle when the presses are run at a high speed. As was heretofore explained, separation of pigment and vehicle results in misting of the ink.

The generation of negative electrical charges on the inking rollers, caused by the friction therebetween, and heretofore mentioned in connection with the misting of ink, also cause the ink to "back-track." By this it is meant that the pigment, when separated from the vehicle upon contact of two similarly charged rollers with each other, tends to back-track through the inking system and redeposit itself in the reservoir or fountain.

The milling of the pigment and vehicle of the ink during the transfer of ink in the inking system, heretofore more fully discussed in connection with the misting of inks, also causes those printing imperfections commonly referred to as "feathering" and "strike-through" and "first impression offset."

Feathering of ink is that printing imperfection characterized by an area which is supposed to be uniformly printed upon being of different shades, due to the fact that in a portion of the area only the ink vehicle is deposited and in other portions of the area the pigment or both pigment and vehicle are deposited.

Strike-through occurs when the ink vehicle and pigment separate. The printing blanket, being coated with an excess of vehicle in certain areas, transfers it to the paper. The vehicle, being more fluid than a homogeneous ink, penetrates entirely through the newsprint, resulting in the impression or image appearing on both sides of the newsprint.

The general object of this invention is to produce a printing ink which will eliminate, or to a large extent overcome, the above-mentioned difficulties which are encountered when ordinary inks are employed; and its primary specific object is to produce a printing ink which has a positive electrical surface charge, instead of being negatively charged, as are the newspaper printing inks now in use.

A further object of the invention is to produce such an ink which is electrically conductive and non-static-forming.

A more particular object is to provide such an ink by incorporating therein a cationic amine and/or one or more other chemicals which cause a change in the composition of the ink from one which has a normal negative charge and which is highly dielectric to one which has a positive charge and a low electrical resistance.

The above and other objects and advantages of the invention will be more fully understood from the following description.

In the normal process of compounding printing inks, an oil or resin which serves as a vehicle, is mixed with the desired pigment, resulting in an ink of the desired type and color. Persons skilled in the art of ink preparation realize that, due to certain properties thereof, not all vehicles can be suitably employed with any and all pigments, but rather, a careful selection must be made between pigment and vehicle, in order to assure a resulting ink of the desired type and color.

As has been heretofore explained, the vehicles and inks commonly employed are dielectrics and possess a negative charge of electrically. However, it should be understood that some vehicles are dielectrics of a higher order than others, and also that the potential of the vehicles

varies from one to another. Therefore, it is not possible to provide any single vehicle which may be employed with all types of pigments, and the treatment of the vehicles, necessary in order that they assume the desired properties, will vary.

When referring to the potential of a liquid, such as an ink or ink vehicle, reference is made to the surface charge thereof, rather than the potential of the entire mass. Since ink vehicles are liquids, a physiochemical change is necessary in order that the surface charge thereof be changed. The change in the surface charge of ink vehicles as disclosed in this invention can best be described as an electrolytic action whereby the dissociation of the molecules in the ink vehicle is effected, causing the creation of cationic surface active agents which rise to the surface to impart a positive surface charge thereto.

By dissociation, the complex molecular structure of the ink vehicle which possesses a negative electrical charge is broken down into two simple molecular structures, one of which possesses a positive electrical charge, the other a negative electrical charge. Those molecules possessing a positive electrical charge are caused to rise to the surface, imparting a positive surface charge to the ink vehicle, and the negatively charged molecules formed by the dissociation are caused to remain beneath the surface.

Since the dissociation of the complex molecular structure of the ink vehicle results in the creation of two compounds of simplified molecular structure, a more stable ink vehicle results therefrom due to the fact that, as a rule, in a compound of simple molecular structure the bond strength between the components thereof is greater than the bond strength of a compound having a more complex molecular structure. The mixing of an ink vehicle composed of two compounds of simple molecular structure with other ingredients is less likely to cause a breakdown of the molecular structure of the ink vehicle than would be the case were an ink vehicle composed solely of one compound of complex molecular structure so mixed. An ink vehicle is always mixed with a pigment. Should the molecular structure of the ink vehicle be unstable, an unwanted chemical reaction between the vehicle and pigment might well result, causing the formation of a chemical compound not suitable for printing.

The preparation of the vehicles used in the inks of my invention is carried out in a resin reactor of that type commonly used in the preparation of ink vehicles, and well known to those persons skilled in the art of ink preparation and formulation.

A typical resin reactor might consist of a multi-mouthed Florence flask. One mouth of the flask would allow carbon dioxide to be introduced into the flask so as to form a blanket above the reagents to prevent the oxidation thereof. Another mouth of the flask could accommodate a reflux condenser which would condense any steam formed by the reaction and conduct it back to the flask. Usually, the condenser is removable from the flask's mouth so that the reagents may be introduced into the flask through said mouth. Another mouth of the flask would accommodate a rod connected to a motor and having a blade on its free end so that the reagents might be stirred.

In the preparation of the vehicle used in the ink of my invention in accordance with a preferred procedure, tall oil and a polycarboxylic acid may be mixed together. The mixture is then heated to a temperature ranging from 225° to 245° C. and is maintained at such temperature for a period of approximately two hours.

It should be understood that refined tall oil is employed only when the resulting vehicle is to be used to produce red, blue and yellow process printing inks, and crude tall oil may be employed when the resulting vehicle is to be used in making black process printing ink. It should be further understood that either saturated or unsaturated polycarboxylic acids may be employed. The

saturated polycarboxylic acids such as malonic, oxalic and glutaric acids engage with the oil in a purely physical mixture and form a soft resin, whereas the unsaturated acids form adducts with the oil and result in a harder resin.

By the term polycarboxylic acid, as used herein, it is intended to include not only those acids with more than two carboxylic groups, but the dicarboxylic acids and their anhydrides as well.

The tall oil adduct or mixture, after being maintained at a temperature between 225° and 245° C. for, say, two hours, is cooled to 160° C. After being cooled, one of the following catalysts may be added thereto, although the addition of such a catalyst is not essential, but rather acts only to hasten the reaction: lithage naphthenate, calcium naphthenate, litharge (lead oxide), dicumyl peroxide, colloidal zinc, lead oleate, dodecyl mercaptan together with tertiary-butyl hydroperoxide and manganese naphthenate, aldehyde amines, dimethyl phenylphosphine and tertiary-butyl catechol. It is to be understood that these catalytic agents may be used separately and, in varying proportions, with conventional metallic ink driers such as cobalt, iron, lead, manganese and copper.

A polyhydric alcohol, such as tripentaerythritol, glycerol, sorbitol, diethylene glycol or ethylene glycol, singly, or in combination one with another, is added to the tall oil adduct or mixture and the reagents are esterified until an acid number of 10 to 25 is obtained. The esterification is maintained until the viscosity of a 50% solution in an aliphatic petroleum hydrocarbon solvent, having a boiling point in the range of 500°–600° F. and a kauri-butanol value of 22.5 to 27.5, such as Standard Ink Process Oil Number 40, Standard Ink Process Oil Number 75, Standard News Ink Process Oil Number 470 or Standard News Ink Process Oil Number 590, is greater than C but less than M on the Gardner-Holdt scale. The oil-modified alkyd resin resulting from the reaction is then reacted with resins and cationic amines or amides, in a manner more fully described hereinafter, to produce a vehicle having the properties referred to hereinabove.

It is to be understood that the above described reaction, wherein the reagents are esterified, may be carried out in the presence of a mutually inert solvent, that is, a solvent which is substantially inert to all of the active components of the reaction, if so desired. The aliphatic petroleum hydrocarbon solvents, having a boiling point within the range of 500°–600° F. and a kauri-butanol value of 22.5 to 27.5 mentioned above are examples of such mutually inert solvents.

Cationic amines or amides are then reacted with oil-modified alkyd resin resulting from the reaction of the above-mentioned components. The cationic amines or amides when reacted with the oil-modified alkyd resin lend two characteristics thereto: (1) they make the vehicle electrically conductive, and (2) they allow said oil-modified alkyd resin to act as to co-solvent, so that resins, which may later be added to the vehicle can be mixed therewith forming a homogeneous mass, rather than precipitating out of the solution. This second characteristic which the cationic amines or amides impart to the oil-modified alkyd resin is referred to as a co-solvent property.

Several examples of the cationic amines or amides that may be reacted with the oil-modified alkyd resin are: aliphatic amides of high molecular weight, such as compounds derived from carboxylic acids by replacing the hydroxyl of the —COOH group by the amino group, an example of such compounds being oleamide (Armid O) referred to in Example III below; and amines such as Amine 220 (1-hydroxyethyl-2-heptadecnyl glyoxalidine) and Atlas G–3780 (cationic polyoxyethylene alkyl amine derivative); also fatty primary amine acetates, fatty nitriles, fatty primary and secondary amines, fatty diamines, and fatty quaternary ammonium compounds.

Certain other metallic salts, as well as certain inorganic salts or electrolytes are compatible with the amines or amides and may be used therewith to make the vehicle much more electrically-conductive. Examples of the metals whose salts might be employed are (1) tin; (2) copper; and (3) zinc. Other more specific examples of salts which might be used are: (1) salts of boric acid; (2) zinc chloride; and (3) magnesium chloride.

After the cationic amine or amide has been reacted with the vehicle, a resin may be added thereto to produce an oil varnish. Examples of resins which may be added are: (1) zinc resinates of rosin; (2) polymerized rosin; (3) Syrian asphalt; (4) Trinidad asphalt; (5) Beta Naphthol pitch; and (6) Gilsonite. Since certain inks are compounded of an oil rather than an oil varnish, those vehicles for use in an ink suitable for use with an oil rather than an oil varnish will not have resins added thereto.

The oil or oil varnish resulting from the above-described procedures may be milled with suitable pigment to produce a printing ink which is electrically-conductive and non-static forming.

An ink produced in accordance with this invention may be readily emulsified, due to the dissociation of the molecules of the vehicle. Ordinarily an ink vehicle is composed of molecules which are hydrophobic in character, whereas a vehicle whose molecules have been dissociated in a manner similar to that herein described, is composed of some molecules which are hydrophobic in character and others that are hydrophilic in character.

When such an ink has been emulsified, the water introduced thereinto tends to hold the pigment of the ink in suspension. When an unemulsified ink prints upon paper, such as newsprint, the oil portion of the ink in which the pigment is suspended tends to enter the body of the paper, carrying the pigment with it. However, when an emulsified ink is used, although the oil portion enters the body of the paper, the water portion, in which the pigment is suspended, stays on the surface, where the pigment remains, even after the water evaporates. When an ink pigment is thus suspended on the surface of the paper, the chance of strike-through is greatly reduced.

The ink of this invention may be emulsified to produce either an oil or a water emulsion. It is preferable to form an oil emulsion, since the action of the oil-soluble emulsifiers, used in oil emulsions, renders the final emulsified product both hydrophilic and hydrophobic in nature, whereas, a water-soluble emulsifier, used in water emulsions, renders the final emulsified product hydrophilic in nature.

To form an oil emulsion from the ink of this invention, a primary oil-soluble emulsifier is added to the vehicle. Primary oil-soluble emulsifiers include: sorbitan mono-oleate; sorbitan monostearate; polyoxyethylene amines; polyoxyethylene sorbitan monostearate; and fatty resin acids.

The water, which is to be added to the vehicle, is mixed with a surface-active agent, so that the pigment added thereto may be uniformly dispersed therein. A lignin sulfonic acid, a surface-active agent derived from wood, could be suitably employed for this purpose. After adding a surface-active agent, a pigment is added to the water and is caused to be dispersed therein.

If desired, a gelling agent may be added to the water-pigment solution before it is added to vehicle. Examples of such gelling agents are: magnesium montmorillonite; hydrous magnesium silicate; gelling clays; carboxy methyl cellulose; hydroxyethyl cellulose; methyl cellulose; and colloidal silica.

The water-pigment dispersion is added to the vehicle and the entire mass is mixed together in a high speed colloidal mill.

It should be noted that the dissociation of the vehicle and the addition of the cationic amines or amides results in the final emulsified product having both hydrophilic and hydrophobic characteristics. When a complex molecule, such as that of an ordinary soap, is broken down into two simple molecules by dissociation, the hydrophilic molecule rises to the surface and the hydrophobic, or oil-soluble molecule, stays beneath the surface, supporting the surface molecules. However, when such a product is emulsified, it assumes both hydrophilic and hydrophobic characteristics, since the surface film, which previous to emulsification was solely hydrophilic, is interspersed with molecules which are hydrophobic. Thus, the oil-modified alkyd resin is capable of absorbing that amount of water found in emulsified inks, absorbing the resin or resins reacted therewith and actually wetting the carbon black which is often used as pigment in black ink.

Since the formulation of ink vehicles in accordance with my invention may vary greatly, owing to the fact that inks for various purposes vary widely in certain characteristics, I have set forth hereinafter some examples which have been proven successful in experimentation.

Example I

900 parts of refined tall oil are mixed with 48 parts of phthalic acid anhydride to which 10 parts of litharge naphthenate are added for catalytic purposes.

The mixture is gradually heated to approximately 280° C., which temperature is maintained for two hours, after which the mixture is cooled to approximately 150° C. After cooling, 125 parts of tripentaerythritol are added to the mixture, and it is reheated to allow the mixture to esterify until an acid number of 14 is reached. The mixture is cooled to 150° C., 100 parts of rosin amine (dehydroabietylamine) are added, and the mixture is stirred for one-half hour.

About 100 parts of the tall oil modified alkyd resin are mixed with 25 parts of an aliphatic petroleum hydrocarbon of high boiling point and low kauri-butanol value and stirred for one-half hour. This mixture is heated to 150° C., 20 parts of a zinc resinated resin is added thereto, and the mixture is stirred for one-half hour. An aliphatic petroleum hydrocarbon of high boiling point and low kauri-butanol value is added. The resulting resin is especially adopted for use in lithographic and newspaper inks.

It should be understood that the portions referred to in this and subsequent examples refer to parts by weight, rather than volume.

Example II

900 parts crude tall oil are mixed with 48 parts of maleic acid anhydride to which 10 parts of litharge are added for catalytic purposes. The mixture is heated gradually to about 280° C. for a two-hour period and is then cooled to 150° C. Thereupon, 125 parts of pentaerythritol are added and the mixture is reheated to esterify to an acid number of about 14. A portion of this tall oil modified alkyd resin, approximately 100 parts, is mixed with about 25 parts of a high boiling aliphatic petroleum hydrocarbon of low kauri-butanol value and held at 150° C. for thirty minutes. A portion of this tall oil modified alkyd resin, approximately 100 parts, is mixed with 100 parts of a fatty amine of chain length of from 8 to 18 carbon atoms. When the mixture is cooled, it solidifies to a paste. The resin and amine is especially adapted to the compounding and flushing of pigments for use in lithographic and news inks (black ink only).

Example III

450 parts of refined tall oil are mixed with 28 parts of fumaric acid and they are reacted in the presence of about 26 parts of Magee 500 (an aliphatic petroleum hydrocarbon of low kauri-butanol value and high boiling point). These are reacted at a temperature range between 220–240° C., for one hour. Then the batch is cooled to 150° C. To this batch is added about 75 parts of pentaerythritol and the contents are esterified until an acid number of 15 is attained. About 100 parts of this

resin solution are mixed with about 25 parts of a paracoumaroneindene resin and 25 parts of Armid O at a temperature of 150° C. for thirty minutes. To this is added 10 parts of calcium naphthenate for catalytic purposes. To this is added 25 parts of Magee 590 (a high boiling aliphatic petroleum hydrocarbon of low kauri-butanol value). The viscosity of the resulting resin solution is 400 poises. It is especially adapted to the compounding of lithographic inks.

Example IV

To 1000 parts of a high boiling point aliphatic petroleum solvent 10 parts of a catinonic amine (high molecular weight aliphatic amine) are added for co-solvent purposes. The mixture is heated gradually to 320° F. and maintained for a one-hour period. Thereupon, 200 parts by weight of asphalt are added and the mixture is stirred for one hour at 320° F. When the mixture has become homogeneous, stirring and heating are discontinued. This resultant resin solution has a great affinity for organic hydrophobic dyestuffs as well as the carbon blacks. The resin is especially adapted for black newsprint inks and can be readily emulsified to tolerate water for printing on high speed news presses.

Example V

To 450 parts of crude tall oil are added 75 parts of phthalic anhydride in the presence of about 450 parts of a high boiling aliphatic petroleum solvent to which 20 parts of a cationic amide are added for co-solvent purposes. Thereupon, about 90 parts of pentaerythritol are added. The charge is heated gradually to about 270° C. and held at about 270° C. or until homogeneous. To this are added 100 parts of an aliphatic petroleum solvent having a high boiling point. The resulting resin solution of low cost is especially adapted for high speed color or black newspaper inks.

Example VI

To 900 parts of crude tall oil are added 48 parts of phthalic acid anhydride to which 10 parts of lead oxide are added for catalytic purposes. The mixture is heated gradually to about 280° C. for a two-hour period and is then cooled to 150° C. Thereupon, 125 parts of pentaerythritol are added and the mixture is reheated to esterify to an acid number of about 14. To this mixture are added 100 parts of a zinc resinated rosin and 100 parts of a high boiling aliphatic petroleum hydrocarbon of low kauri-butanol value and stirred for one-half hour. The resultant vehicle makes an excellent vehicle for dry-offset (lithographic) printing inks.

Example VII

To 1,200 parts of ink, made in accordance with Example IV above, are added 80 parts of a sorbitan monooleate and 47 parts of a polyoxyethylene amine, and these substances are mixed together on a high speed colloidal mill. To 1,750 parts of water are added 20 parts of a lignin sulfonic acid and 162 parts of carbon black. The mixture is stirred to disperse the carbon black in the water. The water-carbon black solution and the ink are mixed together in a high speed colloidal mill. In this manner an emulsified ink having the desirable properties above described is produced.

The conductive ink of my invention accomplishes many practical results. Among the results which are accomplished by use of the ink of my invention are: clearer and brighter printing; more uniform tonal quality in the printing, owing to better pigment dispersion throughout the vehicle; reduction in the time spent cleaning up the press room, owing to the fact that the ink does not mist; and color reproductions of greater clarity and sharpness, owing to the fact that smearing of the three colored inks is eliminated, thus preventing any overlapping of colors.

Since certain variations may, of course, be made in the compositions and procedures above described without departing from the spirit and scope of the invention, it is intended that the foregoing specification shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. A cationic, electrically-conductive printing ink comprising a pigment and a vehicle composed of the reaction product of an oil-modified alkyd polycarboxylic acid-polyhydric alcohol resin and an aliphatic primary amide of high molecular weight which amide is surface active and of the cationic type.

2. A method of producing a cationic, electrically-conductive printing ink, comprising mixing tall oil with polycarboxylic acid and polyhydric alcohol, to form an oil-modified alkyd resin; adding a member of the group consisting of surface active amines of the cationic type and surface active primary and secondary amides of the cationic type to said oil-modified alkyd resin; and milling the resulting vehicle with a pigment.

3. A cationic, electrically-conductive printing ink comprising a pigment and a vehicle composed of the reaction product of an oil-modified polycarboxylic acid-polyhydric alcohol alkyd resin and a member of the group consisting of surface active amines of the cationic type and surface active primary and secondary amides of the cationic type.

4. The printing ink of claim 3 having a metallic salt added to said vehicle to increase the electrical conductivity thereof.

5. The printing ink of claim 3 wherein said resin is formed from (1) an adduct of tall oil and an unsaturated carboxylic compound and (2) a polyhydric alcohol selected from the group consisting of pentaerythritol, tripentaerythritol, glycerol, sorbitol, ethylene glycol and diethylene glycol.

6. A cationic, electrically-conductive printing ink comprising a pigment and a vehicle composed of the reaction product of an oil-modified polycarboxylic acid-polyhydric alcohol alkyd resin and a fatty primary amine acetate, said acetate being surface active and of the cationic type.

7. A cationic, electrically-conductive printing ink comprising a pigment and a vehicle composed of the reaction product of an oil-modified polycarboxylic acid-polyhydric alcohol alkyd resin and a fatty diamine, said diamine being surface active and of the cationic type.

8. A cationic, electrically-conductive printing ink comprising a pigment and a vehicle composed of the reaction product of an oil-modified polycarboxylic acid-polyhydric alcohol alkyd resin and a fatty quaternary ammonium compound, said compound being surface active and of the cationic type.

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