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INKS AND VEHICLES THEREFOR

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With so-called "heat-set" inks, useful for letterpress printing, a great excess of more or less toxic or noxious liquid solvent or diluent must be driven off the printed sheet almost instantaneously. Complicated, costly and bulky heating, drying and ventilating equipment are required for the purpose, to which but few presses are adapted and, moreover, the intense heating required in such practice may adversely affect the folding, sealing, scoring and bending properties of the paper. Though the solvent of "heat-set" inks must be substantially blasted from the printed sheet, such ink nevertheless dries in air, necessitating frequent interruption of operations for washing hardened ink from the press.

So-called oxidizing inks having vehicles of drying or semi-drying oils that set by oxidation, require a day or more for the printed sheet to dry sufficiently for handling in subsequent operation such as printing a further color, cutting, binding, or folding and moreover the practice of "winding" must be resorted to to prevent adhesion or sticking of the sheets due to the oxidation of the vehicle and to mitigate the objectionable odor of the finished product. The addition of but a small proportion of gums or resins has been feasible in an effort to improve finish, adhesion and hardness, and to shorten the drying time, for larger proportions if soluble at all in such oils, result in a tacky and excessively heavy body. The drying time of oxidizing inks with the use of such gum or resin ingredients has been shortened from twenty-four hours or more down to in the neighborhood of an hour. But even were it possible, with the addition of such gum or resin to accelerate the drying time down to a period measured in seconds, rather than minutes, the evil of offsetting, smudging or sticking would still exist and slip sheeting, spraying or like expedients would still have to be resorted to, as would the practice of "winding," and the operation would have to be frequently interrupted to permit the press to be cleaned and washed, due to the drying of the ink thereon.

Among the objects of the present invention are to provide a printing ink which admits of multi or process color printing in a single pass through almost any multi-color press available at the present time and which admits of single color printing on any press, all without any danger of

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smudging, sticking or picking and which, following the application of heat, as for instance, from one or more gas burners at the delivery end of the press, accomplishes delivery of the imprinted sheets in dry or set condition at all speeds of which the press is capable up to 5,000 or more multi-color printed sheets per hour, with the abolition of all slip sheeting, spraying, racking, traying and also of the practice of "winding" the sheets, and with the elimination of costly, bulky, elaborate equipment for heating or for ventilation, yet without hazard due to combustible or toxic or noxious ingredients.

Another object is to provide a practically odorless printing ink, devoid of nitrocellulose or other highly inflammable ingredients, which may be stored for long periods without deterioration, which will not dry or cake on the press, and thus avoids the need for frequent washups and which develops no tackiness in drying.

Another object is to provide a vehicle for an ink of the above type, having the desired fluidity which may be stored for long periods and without deterioration due to skinning, hardening, livering or drying, despite the fact that the vehicle has a solvent content so small as substantially to be completely absorbed by the paper as the imprint is hardened or set.

Another object is to provide a vehicle for an ink of the above type which admits of the use as the coloring medium not only of conventional pigments but in lieu thereof of various dyes, by which economies and novel effects are attained as are other advantages including greater expedition in setting or drying and a homogeneous imprinted film or impression with greater coverage.

This application is a continuation-in-part of our copending case, Serial No. 369,122, filed December 17, 1940, now abandoned.

The invention involves the use of a new vehicle comprising essentially a partly polymerized alkyd resin, dissolved in a small proportion of solvent that is substantially non-volatile at room temperature, which vehicle will carry dyes in solution therein in proportions fully adequate for any density of coloration, or alternatively will carry in dispersion the pigments commonly used in printing inks, and which ink will instantly set, harden, condense or polymerize when heated,

the small amount of solvent being substantially absorbed by the sheet being imprinted.

The vehicle in a desirable embodiment is a resin made from a mixture of saturated dibasic acid, polyhydric alcohol and higher fatty acid, the mix being partially polymerized to predetermined degree, so that it is semi-plastic and not readily flowable at room temperatures. The semi-plastic prepared according to our teachings (that are more fully set forth hereinafter), lends itself to thinning to the required flowability for printing inks, by dissolving in ordinary inexpensive petroleum hydrocarbon, preferably of the aliphatic type that is substantially non-volatile at room temperature.

The dibasic saturated acid may be succinic, adipic or homologous acid stable under heat, but for general application phthalic anhydride is preferred by reason of its low cost. An unstable acid such as malic which decomposes upon heating to the unsaturated maleic type is not within the scope of the designation "dibasic saturated acid stable under heat". The higher fatty acid ingredient may be any ordinary vegetable oil fatty acid which is commercially available. Such fatty acids are commonly derived from soy beans, linseed, hempseed, castor, menhaden, tung or perilla oil and include largely oleic, linoleic and linolenic acid. The polyhydric alcohol may be a glycerol, a glycol, erythritol, pentaerythritol, mannitol or the like, but for general application glycerol has been found to be most economical at the present time.

We have found, after long experiment, that the vehicle base of desired high solubility in aliphatic hydrocarbon solvent that is non-volatile at room temperature, must be of substantially critical proportions, processed in a definitely controlled manner. Specifically we have found that the desired product results when substantially 3.5 moles of trihydric polyhydric alcohol, 2.75 moles of phthalic anhydride and from 1.0 to 1.5 moles of vegetable oil fatty acid are polymerized to that predetermined degree which is attained by slowly heating with agitation, taking approximately one hour to reach 230 degrees C. and then continuing to heat at approximately that temperature for three hours and fifteen minutes more with the introduction of inert gas. The active radical of the polyhydric alcohol being the hydroxyls, the number of hydroxyls in 3.5 moles is 10.5 from a molar standpoint. With polyhydric alcohols of lesser or greater hydroxyl value, the molar equivalents will be correspondingly greater or less to afford the same hydroxyl value. We are not familiar with any way of defining the degree of polymerization except by some procedure such as that set forth for attaining it.

One particular formula which in practice has been found especially suitable when processed as above set forth, is made up of the following ingredients in the following proportions by weight:

	Parts
Phthalic anhydride	81
Glycerine	64
Soy bean fatty acids	81

The partially polymerized semi-plastic product resulting from the foregoing process enters easily into solution in ordinary aliphatic hydrocarbon solvents not volatile at room temperature. In fact the 226 parts by weight of the foregoing formula readily dissolve in 110 parts by weight of an inexpensive aliphatic hydrocarbon of boiling range between 500° to 600° F. The resultant

vehicle, although it contains 65 per cent or more of solid matter and only 35 per cent or less of solvent, nevertheless has the required low viscosity for a printing ink vehicle. That a product including these ingredients involving the small fatty acid content prescribed, could be soluble to such extent in such aliphatic hydrocarbons was unexpected both by those skilled in the printing ink art and those skilled in the resin art. That property is an important factor in the utility of the vehicle as will appear more fully hereinafter.

Where a considerably larger proportion of fatty acid is used than above specified, while the solubility of the resultant vehicle base is enhanced, it dries slowly and therefore becomes unsuitable for purposes of the present invention. On the other hand, where a lesser amount of fatty acid is used than herein specified, the resultant product becomes practically insoluble in aliphatic hydrocarbons and could be dissolved only in the more potent, more volatile and more costly solvent, with the objections above pointed out.

If more heat is introduced into the mix than above specified, the polymerization will be carried on to such degree that more solvent will be required than can be absorbed by the paper in the absence of the evaporation equipment with which the present invention dispenses. On the other hand, if less heat be used, then the polymerization will be carried on only to such extent that even though less solvent be adequate for solution of the product, the printed surface will remain tacky, and the consequent higher acid number results in livering of color lakes.

The vehicle of the specifications set forth has one other surprising property of high utility in printing inks and the like. It is an excellent solvent for non-water soluble dyes that heretofore have been found to be soluble only in expensive, potent solvents such as glycol derivatives, esters or ethers, alone or in combination with benzene hydrocarbons such as benzene, toluene, xylene or the like. Though of the ingredients as such of our vehicle, only the fatty acid is a solvent for dye bases, our vehicle composed of these ingredients, notwithstanding its extremely low acid number, readily dissolves, to the surprise of those skilled in the art, relatively large proportions of all color base dyes of the diaryl methane, the triaryl methane and the oil soluble azo types. Among these are those of negrosine, rhodamine, Victoria blue, malachite green and diazaphine yellow base. In fact such dyes can be used in lieu of instead of merely as a supplement to pigments. In general the amount of dye used is not less than one (1) and not more than five (5%) per cent of the weight of the vehicle to secure the maximum degree of coloration required, but considerably larger proportions of most of said dyes are soluble in the vehicle without danger of being precipitated at low temperatures. Since the vehicle of the present invention is not acid in character, it admits of admixture also with color lakes which would liver in an acid environment. The dyes could be dissolved in the vehicle after preparation of the latter, or after preparation of the partially polymerized base and before adding the solvent.

The dye has many advantages over the pigment coloring agent. Greater coverage is obtained since the coloring pervades the film and lacks the discrete particles of pigment inks. The imprinted film having no hard or gritty particles is homogeneous and will not scratch or rub.

By reason of the absence of vehicle absorbent pigment particles, more expeditious drying or setting of the dye colored ink results. Furthermore, the translucency of many dyes renders them more suitable for certain process color printing effects. Finally, the absence of solid pigment particles obviates the filling of the screen in the printing plate and the press requires less frequent washing and cleaning than where pigment inks are used.

The vehicle set forth may be stored in containers indefinitely without change in its physical or chemical characteristics and indeed can be exposed to the open air regardless of temperature without hardening, drying or other deterioration. It may be admixed by the manufacturer or by other processors with the necessary color and other ingredients to produce the printing ink as required, with a solid content of preferably not less than 65 per cent.

The formula above specified could be modified, if desired, by reducing the soy bean fatty acid ingredient from 81 parts to as little as 54 parts. The ingredients of the modified formula are processed exactly as above set forth to produce the partially polymerized resin. This, however, is not as readily soluble in petroleum hydrocarbon solvent as is the formula with the larger amount of fatty acids. The solution of the resin in the solvent is brought to pass by constant agitation of the mix until slowly cooled to room temperature.

The ink of the present invention, whether in the pigment or the dye embodiment may, depending upon the particular type of printing to be done and the characteristics desired, be admixed with any or all of various materials commonly used in the manufacture of printing inks such as toners, extenders, fillers, wetting agents, waxes, compounds, thinners or reducers and driers, properly dispersed in the vehicle.

In use of the ink of the present invention, the thin film imprinted upon the sheet in the ordinary manner dries or sets instantly as it passes a heater beyond the impression cylinder or platen of the press, the minor amount of solvent in the ink being in large part absorbed by the paper. Where a gas flame is used for the purpose, sufficient water vapor is evolved as a product of combustion to prevent dehydrating the paper sheet or breaking down the fiber, so that it remains flexible and will not crack in subsequent folding or bending. Such heater of simple, compact and inexpensive form is disclosed in the Cole Patent No. 2,153,325 of April 4, 1939. The heat causes the partially polymerized resin of the vehicle to "kick over" that is materially to advance or to complete its polymerization, so that the imprint is substantially completely dried or set by the time the sheet leaves the press. Any small excess of solvent beyond what the paper will absorb, will be incorporated in the polymerized resin or will evaporate. The imprinted paper leaves the press in dry or set condition. The resin in setting or drying under heat incorporates the pigment or dye with it, to produce a waterproof imprint, so intimately incorporated with the paper that it does not rub off.

While the ink thus dries or hardens readily under the heat of the gas flame, it will not harden or dry at room temperature. This is due to the fact that the partially polymerized resin is of the type the polymerization or condensation of which will not progress in the solvent

under atmospheric conditions and also because the solvent is substantially non-volatile at room temperature. Therefore, the ink may readily be removed from the printing form and rollers of the press, without the difficulties incurred with so-called evaporating inks or with oxidizing inks which progressively harden when exposed. For this reason the ink can be stored indefinitely without deterioration and will not harden or dry even though exposed to the air for some time.

By reason of its high solid content the ink can be laid down upon the paper in multi or process color printing in one pass through an appropriate press, without the necessity for drying each color application before applying the succeeding one. The gas heating equipment at the delivery end of the press hardens, sets or polymerizes the vehicle of the ink, whether applied in a single or in multiple impressions. Sheets delivered from the press at the rate of even 5,000 or more per hour may thus be directly stacked upon each other without danger of offsetting, smudging, sticking or picking, with the elimination of slip sheeting, spraying, racking, traying or other expensive expedients intended to mitigate those evils. The ink being substantially completely set as the sheet leaves the press, no material further reaction occurs in the stack or roll of imprinted paper. The danger of sticking together that occurs with oxidizing inks is non-existent and the practice of "winding" resorted to with oxidizing inks is not necessary, and the printed product has no objectionable odor. Thus, the excess space required in press rooms for work in process of drying or setting, and amounting in many cases to thirty per cent of the total floor space, may be dispensed with, without incurring the limitations and hazards of costly and bulky installations necessary with the so-called "heat-set" or evaporating inks.

While the invention is especially advantageous for letterpress printing in single, multi or process color printing, it is not restricted to this use, but can be used on other types of presses with highly satisfactory results. In certain types of printing, especially upon soft or open surface paper stock, the imprint will leave the press sufficiently hard and set, even though the heater be omitted.

The ink of the present invention may be used advantageously in lieu of conventional linseed oil vehicle ink and with economies and improved results. Where the heater is dispensed with and no means is provided for kicking over the partially polymerized resin, a suitable conventional siccative would be added to promote drying.

While the vehicle and ink as above described meets the most exacting requirements of the printing art, it is satisfactory for many purposes to reduce the cost by incorporating in the vehicle base a substantial proportion of ester gum, but if too great a proportion is used, the ink would tend to remain sticky on the sheet, so that in time the film would break or crack. Ester gum is prepared by the esterification with glycerin or other polyhydric alcohol of abietic acid, usually derived from colophony or rosin which is composed largely of such acid and its anhydride. In some cases as much as three parts by weight of such ester gum may be used with one part of the partially polymerized vehicle base previously described and one part of the petroleum hydrocarbon solvent. The viscosity of the resulting vehicle in this case is considerably lower than that of a vehicle prepared either with the alkyd resin

or the ester gum alone in the same proportion of the same solvent.

One particular formula of the vehicle last set forth is made up of the following ingredients in the following proportions by weight:

Alkyd resin composed of

	Parts
Phthalic anhydride	27
Glycerine	21
Soy bean fatty acid	27

The 75 parts of alkyd resin partially polymerized as above set forth, are dissolved in some 37 parts of aliphatic hydrocarbon and

Ester gum composed of

	Parts
Abietic acid	135
Glycerine	17

The 150 parts of ester gum are dissolved in some 75 parts of aliphatic hydrocarbon.

The mixture of alkyd resin and ester gum solutions is found to have a viscosity lower than either of the component solutions. The same is true if the ratio of ester gum to alkyd resin is changed from that of the above illustrative example to as much as 3 to 1.

The term "polymerization" as used in the broader claims is not confined to any closely limited technical meaning, but defines the molecular aggregation or conglomeration that occurs in the formation of plastic or semi-plastics from raw materials, regardless whether this be due to polymerization in the narrow sense of the term or to other chemical or physical action, such as condensation or combination of various actions.

While the invention has been described in its application as a printing ink for which purpose it has outstanding utility, it will be understood that it is useful in other branches of the graphic arts, for imprinting not only paper but other materials including textiles, wood, metal, etc.

As many changes could be made in the above vehicle, ink and process and many apparently widely different embodiments of this invention could be made without departing from the scope of the claims, it is intended that all matter contained in the above description, shall be interpreted as illustrative and not in a limiting sense.

Having thus described our invention what we claim as new and desire to secure by Letters Patent of the United States is:

1. A vehicle for a printing ink, consisting of substantially two parts by weight of partially polymerized resin dissolved in about one part by weight of aliphatic hydrocarbon solvent that is substantially non-volatile at room temperature, said partially polymerized resin being made by reacting a mixture consisting of 2.75 moles of phthalic acid anhydride, 1 to 1.5 moles of vegetable oil fatty acid, and polyhydric alcohol of hydroxyl value substantially equal to that of 3.5 moles of glycerol, and in which the alcoholic hydroxy groups are the sole reactive groups, said resin being partially polymerized by slow heating of the said ingredients with agitation, taking approximately one hour to reach 230° C. and then continuing to heat the same approximately at that temperature for three hours and fifteen minutes more.

2. The vehicle recited in claim 1 which includes not more than three parts by weight of ester gum to one part of the resin, said ester gum being also dissolved in aliphatic hydrocarbon solvent.

3. The combination recited in claim 1 in which the aliphatic hydrocarbon solvent has a boiling range between 500 degrees and 600 degrees F.

4. A vehicle for a printing ink consisting of not more than three parts by weight of ester gum to one part of alkyd resin, said ester gum and resin being dissolved in aliphatic hydrocarbon substantially non-volatile at room temperature, said solution being substantially 65% of the resin and gum to substantially 35% of the solvent, said alkyd resin being made by reacting a mixture consisting by weight of substantially 21 parts of glycerin, 27 parts of phthalic acid anhydride, and 27 parts of vegetable oil fatty acid, said resin being partially polymerized by slow heating of the said ingredients with agitation taking approximately one hour to reach 230° C. and then continuing to heat the same approximately at that temperature for three hours and fifteen minutes more.

5. A printing ink consisting of substantially two parts by weight of resin dissolved in one part by weight of aliphatic hydrocarbon solvent that is substantially nonvolatile at room temperature, said solution constituting a vehicle having dissolved therein coloring matter consisting of basic dyes selected from the group consisting of diaryl methane, triaryl methane, and the oil soluble azo dyes, said resin being made by reacting a mixture consisting of 1 to 1.5 moles of vegetable oil fatty acid, polyhydric alcohol with hydroxyl value substantially equal to that of 3.5 moles of glycerol and in which the alcoholic hydroxy groups are the sole reactive groups, and 2.75 moles of acid compound selected from the group consisting of phthalic acid anhydride and stable saturated carboxylic dibasic acid, in which the carboxyl groups are the sole reactive groups, said resin being partially polymerized by slow heating of the ingredients with agitation taking approximately one hour to reach 230° C. and then continuing to heat the same approximately at that temperature for three hours and fifteen minutes more.

6. A printing ink consisting of substantially two parts by weight of resin dissolved in one part by weight of aliphatic hydrocarbon solvent that is substantially non-volatile at room temperature, said solution constituting a vehicle having dissolved therein coloring matter of from one to five per cent of the weight of the ink, and consisting of basic dye bases selected from the group consisting of diaryl methane, triaryl methane, and the oil soluble azo dyes, said resin being made by reacting a mixture consisting of 2.75 moles of phthalic acid anhydride, 1 to 1.5 moles of vegetable oil fatty acid, and polyhydric alcohol of hydroxyl value substantially equal to that of 3.5 moles of glycerol, and in which the alcoholic hydroxy groups are the sole reactive groups, said resin being partially polymerized by slow heating of said ingredients with agitation taking approximately one hour to reach 230° C. and then continuing to heat the same approximately at that temperature for three hours and fifteen minutes more.

7. A printing ink consisting of a vehicle base comprising one part of resin to not more than three parts by weight of ester gum, said printing ink having a vehicle comprising substantially 65% of said vehicle base dissolved in substantially 35% of aliphatic hydrocarbon substantially non-volatile at room temperature, said vehicle having in solution therein coloring matter of from one to five per cent of the weight of the ink, and consisting of basic dye bases selected

from the group consisting of the diaryl methane, triaryl methane, and the oil soluble azo dyes, said resin being made by reacting a mixture consisting by weight of substantially 21 parts of glycerin, 27 parts of phthalic acid anhydride and 27 parts of vegetable oil fatty acid, said resin being partially polymerized by slow heating of said ingredients with agitation taking approximately one hour to reach 230° C. and then continuing to heat the same approximately at that temperature for three hours and fifteen minutes more.

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