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Drying Oils in Printing Inks

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TWO TRENDS IN THE UNITED STATES have had a tremendous impact on the printing ink industry, mass communication and mass merchandising. There is evidence of these two trends on the newsstands and in the local supermarket every day. It is possible, with new printing equipment and paper stocks, to print a magazine in full color and to issue this magazine weekly with millions of copies. Likewise newspapers printed with some color are much more attractive and carry greater sales impact to the reader. Book-of-the-month clubs, pocket books, and other publications are constantly increasing the market for printing inks.

Mass merchandising has changed the method of purchasing for practically everyone. In today's supermarkets and department stores almost everything is prepackaged and ready for sale to the customer. Product identification is, of course, supplied by printing inks.

These two changes and the resulting increase in the volume of printing have brought about a revolution in printing speeds. To increase production, faster and faster press speeds have been used. The higher speeds have made the inks used a few years ago unsatisfactory for today's new high speed presses. New printing surfaces such as polyethylene, cellophane, polyvinyl chloride, polyesters, and others have brought up a host of new problems, such as drying and adhesion, calling for some entirely new formulations in ink. In view of these changing conditions the printing ink manufacturer finds it necessary to carry a large research program to fit tomorrow's inks to improved presses and to new papers and films.

Printing Processes

The requirements for a printing ink are based upon the method of application. There are four main methods of applying ink to the surface to be printed; they are letter-press, gravure, lithography, and flexography.

Letter-press, as the name indicates, is the pressing of a surface to be printed, usually paper upon raised letters or type. It is the oldest and by far the most important method of printing. Press sizes range from a small hand-fed press to giants that print from rolls of paper at speeds well over a thousand feet per minute and, in some cases, approaching two thousand feet per minute. Depending upon the speed of the press and the method of drying, the ink will be tailor-made for the particular press.

Gravure, or more specifically rotogravure, and again the name is self-explanatory, is a process of printing from a rotating engraved or etched cylinder. Historically gravure was first used in England for the printing of fabrics. It is now used for printing magazines and other large-volume printing. In contrast to letter-press, where the ink is carried upon a raised surface before transfer to the surface to be printed upon, rotogravure carries the ink in a recess or a cell. By varying the cell depth, gradations in the density of the color can be obtained. This gives rotogravure an advantage over other types of printing since the density can be varied from a soft highlight to a dense solid.

The graven or etched cylinder is rotated directly in the ink. The excess ink is then wiped off by a "doctor blade," which oscillates across the cylinder, wiping it clean. Since the ink is in contact with metal only and there is no rubber distribution-system involved in gravure, strong solvents such as ketones, esters, or aromatic solvents can be used in the ink formulation. Because of the simple distribution system very volatile solvents can be used, permitting rapid drying by evaporation on nonabsorbent stocks. The ability to use these strong solvents enables the ink maker to use a wide selection of film formers such as nitrocellulose, chlorinated rubber, vinyls, polystyrene, etc. Gravure drying is always by evaporation of solvent and not by oxidation.

Lithographic Method of Printing

Of the major printing processes, lithography occupies a major position both as to production and quality. Lithography differs from letter-press in essentially three ways. The printing plate used in lithography is flat (level) or very slightly etched. The printing process is accomplished in a more circuitous manner, that is, the ink is not transferred directly from the plate cylinder to stock but instead is transferred to a blanket cylinder, which in turn transfers the ink to the stock. The process is based on the principle that oil and water do not mix. In practice the printing plate is so treated that only a portion of the plate is made ink-receptive, *i.e.*, that portion of the litho-plate which does not contain the printing image is made nonreceptive to ink by the application of water to the plate. This approach has undergone further refinements in that, in some instances, ink receptivity and nonreceptivity of the plate are established through the use of specific alloys.

Flexographic Method of Printing

Flexography is another method of printing and can be called a variation of letter-press printing.

Starting as "aniline printing" at the English firm of Bibby, Baron, and Sons Ltd., a paper bag manufacturer, almost 70 years ago, it has grown very rapidly in the past few years. The ink consistency is similar to gravure, and again very volatile solvents are used. Because of the rubber or flexible plastic plates, the type of solvent is limited as well as the film formers that can be used. The plate is not as expensive as metal plates and is limited to about 80 lines per inch so that sharp reproductions are not possible. It is particularly suited for plastic film and polyethylene, also for foil.

Various Types of Binders for Printing Inks

Each of these four methods of printing requires a different type of ink, and among these types there will be many thousands of variations, tailor-made for the particular press, paper, film, coverage, and even weather conditions. This is one of the reasons the printing ink industry is on a "prescription" basis. Perhaps the only standardized ink, if it could be called that, would be news ink. Even here with a two-ingredient ink, mineral oil and carbon black, there are many variations in formulation.

Binders for letter-press inks cover a wide range of formulation, from a bodied linseed oil to resin oil and resin solvent and combinations of these. The type of binder will depend upon the press and the surface to be printed upon. General requirements are that the ink be fluid enough to be easily distributed by the rollers of the press upon the printing plate. After being transferred to the plate, it must be high enough in viscosity so that it will stay put on the type and not run off or plug the half-tone screen. Transfer qualities from the plate to the stock must also be good. The transfer of the ink is better on an absorbent paper than upon a nonabsorbent surface. Transfer fortunately is usually not a problem.

Letter-press inks can be gloss, steam-set, heat-set, or oxidizing. Also in some cases combinations of these are made. The binder imparts to the ink its method of drying and appearance, whether gloss or flat, after drying.

Letter-press gloss inks are generally made by using an oil-resin vehicle with the addition of a few per cent of kerosene or other solvent to reduce viscosity and obtain a printable viscosity.

The formulating of gloss vehicles can be quite difficult. The solution of the resin in the oil must be border-line. This is necessary since, upon printing, the paper will absorb a large percentage of the oil portion of the vehicle and leave the pigment resin on the surface of the paper, giving a good gloss to the finished product. The setting speed must be carefully controlled since if the ink sets too fast, it will not have time to level and produce a maximum gloss. Conversely if it sets too slowly, the vehicle and resin penetrate into the stock with a resulting loss of gloss.

Steam-set inks are also used in letter-press, and their binders are glycol-resin solutions. This type of ink is used where low odor is a requirement, as on bread wrappers and food containers. As with gloss inks there is a border-line solubility. However this border-line solubility is based upon a three-phase system: glycol-water-resin. As the water is increased, the solubility of the resin is lowered and finally precipitates the pigment and resin. Moisture is supplied at the press by blowing steam upon the freshly printed ink. As soon as the critical point is reached, the resin starts to precipitate and carries along the pigment. The glycol is then absorbed into the paper, leaving the pigment and resin on the surface of the paper. Since the precipitated resin-pigment cake does not fuse to form a continuous layer, steam-set inks are usually lacking in gloss. Some progress has been made by using resins of low melt-points or fast solvents. However these are not the whole answer to gloss steam-set inks. The idea of low melt-point resins can only be carried so far since they will cause sticking when the paper is rewound after printing.

Heat-set inks are another type of ink applied by letter-press and are made with a resin-solvent vehicle. Solvents are of a hydrocarbon type with an aniline value of 150–180. The resins are of high melt-point type, usually in the range of 110–130°C., and are of such a nature as to be soluble in the low-solvency hydrocarbon solvents. These can be either ester gum or a modified-phenolic or a maleic-modified resin. The polyol is usually glycerine or pentaerythritol. For special uses the polyol can be of higher functionality, but this is usually not necessary. A small amount of drying oil, such as linseed, may be included for wetting the pigment. This will later oxidize and give some added scuff-resistance to the printed film. The heat-set inks are, of course, quite simple in construction and are used for publication work.

Oxidizing inks are used for letter-press printing of cartons. It is sufficient to say that they were at one time practically the only type of ink made and are still very important.

Lithographic Inks

Lithographic inks are heavier in viscosity than letter-press inks. Again they can consist of resin-drying oil or resin solvent, or a combination of these materials. Metal decorating inks are usually based upon oxidizing alkyds. All of these inks must be insensitive to water and resist emulsification. Vehicles for the lithographic process should be of low acid value to prevent reaction with pigments and subsequent soap formation that causes water sensitivity. Also the driers must be carefully selected and must be as nearly neutral as possible.

Heat-set lithographic inks are formulated in a manner similar to letter-press heat-set inks. However they must also be difficult to emulsify and resist scumming.

Gravure Inks

Gravure inks differ from letter-press and lithographic inks. In contrast to the latter, they must have low surface-tension so they can quickly fill the cavities of the engraved cylinder and produce a smooth print.

Gravure inks consist of resins dissolved in a volatile solvent. Usually the resin, solvent, and pigment are loaded into a ball mill and ground together. This results in finished ink in one operation and, if properly done, in saving of time. It is also possible first to disperse the pigment in the resin on a two-roll rubber mill and later dissolve this chip with a volatile solvent in a ball mill for a finished ink. Since the pigment is dispersed in the resin under very high shear, it is very well dispersed. This results in increased gloss and transparency that is difficult or impossible to achieve with ball-mill grinding.

Gravure inks are also printed on a variety of surfaces. Since this requirement will take many types of binders that are soluble in different solvents, all classes of inks have been typed in terms of miscibility and dilutability. These types are designated by letters of the alphabet such as A, B, C, D, E, to name a few, also W. As an illustration, Type A inks are used in publication work and are dilutable with petroleum naphtha, such as V.M.P. naphtha. Type C inks contain nitrocellulose and are used for printing on cellophane, some acetates, boxboard, and foil; they are reducible with esters or ketones. Type E is a specialty ink made with alcohol-dilutable resins. Type W are the water-dispersible type and are dilutable with water or alcohol.

This covers, in a very general way, the basic types of printing and some of the requirements that an ink must meet.

Drying Oil Vehicles—General

Inks made with drying oils have been used for a long time. The English and the Dutch ink-makers were the first to recognize the full value of drying oils in inks. Linseed oil served as the basic ingredient in the early commercial inks. The Dutch ink-makers also incorporated small amounts of rosin into their ink varnishes. In contrast, the English, with an eye on cost, would often blend whale oil into their linseed vehicles. This practice, while accomplishing a saving, produced an inferior type of product for it resulted in slow-setting, greasy inks that lacked good printing qualities.

The Dutch also realized and appreciated the benefits obtained with polymerized drying-oil vehicles. They often cooked or boiled their oils to obtain oils of varying viscosities, a practice the British did not employ until some time later. When compared with the British, the Dutch processed their varnish in a superior manner; Dutch printing vehicles were clarified by adding litharge to the hot varnish; the resulting product was then strained.

The 18th century saw, in addition to linseed, use of nut oils, rape seed, and hemp oil.

Despite tremendous technological advances the basic practice of the Dutch is followed today. Printing ink vehicles seldom consist of 100% oil; current drying-oil vehicles are generally combined with resins, and, depending on the properties desired, the type of oil and resin will vary.

Printing-ink vehicles which dry by oxidation and polymerization most nearly resemble the vehicles employed in surface coatings. Although printing ink made with a drying oil dates back almost 500 years, the superiority of this type of vehicle is made evident by the fact it still must be considered the No. 1 vehicle for letter-press and offset printing.

Oils Used—General

China wood oil is used in ink vehicles whenever rapid drying is required. However, because of China wood oil's fast bodying-rate, few drying-oil vehicles are made exclusively with C.W.O. Rather it is most frequently used in varying amounts to upgrade the drying rate of other drying-oil vehicles. Again, when alkali-proof inks are required, such as those for soap wrappers, China wood is the favored oil. In these instances the drying portion of the vehicle invariably consists of 100% China wood oil. It is also used to advantage in inks that must possess good scuff resistance, that is, inks which are to be used for printing cartons, etc. Gold and silver metallic inks require vehicles which must dry rapidly and afford good leafing and binding characteristics. C.W.O. again is the favored oil for this type of ink. It not only confers to the ink the above properties but also provides metallic inks that possess good brilliance when dry.

Linseed Oil

Linseed oil is by far the most widely used drying oil in printing ink vehicles, and rightly so, for it combines in one oil many properties that are of vital importance if one is to successfully formulate quality P.I.: good rate of dry, good gloss, hard and good binding films, etc.

A term widely used in the printing ink field is lithographic varnish. This is nothing more than bodied linseed oil. The viscosity does vary, depending on the end-use. The viscosity grades commonly encountered run from 1.8 poises to 200.0 poises, corresponding on the lithographic scale from 000 to #6.

It seems appropriate at this time to digress a moment and briefly mention oil viscosity and its relation to and effect on the various types of printing inks currently used. Oil viscosity will of course vary, depending on the properties desired in the finished ink. These properties, in turn, are somewhat fixed by the type of stock to be printed and the particular type of printing process to be employed, whether letter-press or offset.

It is a general rule that inks should be as tacky as the grade of stock and type of press will permit. For example, for hard, nonabsorbent stock, such as bond, it is recommended that a hard-drying vehicle with a lithographic body on the high side be used: #5 or #6 blended back if necessary with #1. For coated stocks, particularly when the coating is not anchored too firmly, inks prepared with light-grade lithographic varnishes (#0 and #1) are best. This is necessary so that the ink will not pick the coating.

Pursuing vehicle viscosity-paper relationships a bit further, it is not difficult to visualize that ink hold-out is directly related to vehicle viscosity. When the viscosity of the vehicle becomes too low, the vehicle is absorbed to such an extent that, for all the protection it affords to the pigment, one might as well have tried printing straight pigment. Interfibrous space in the paper however is desirable for it does serve in a sense as an air reservoir upon which the drying oil can draw to speed drying. Linseed oil is used in two forms in ink vehicles, either as a dark oil or as a light oil. The dark oil, which is blown to obtain proper viscosity, is generally used in inks where color is not too important. There are several advantages connected with its use, of which the following are important. Because of the more polar nature of the dark oil, it provides for better wettability of pigments, resulting in inks which generally dry faster, produce more gloss, and bind to the stock somewhat more tenaciously than the light linseed oil. These advantages coupled with its cheaper cost provide any printing-vehicle manufacturer with a tempting package. In favor of the light oil it can be said that the light oil produces less thixotropic inks. Since good flowing inks are desired so that they may distribute and transfer properly on the printing press, this can be an important consideration. Again the light oil variety of linseed produces somewhat more stable inks; there is less tendency for pigment/vehicle interaction on storage.

Soybean Oil—General

Soybean oil is finding increasingly wider acceptance in the manufacture of printing-ink vehicles. This can be attributed to the excellent availability of the oil and its lower cost.

Soybean oil, as such, is seldom used for it yields very slow-drying inks which cure to very soft films. However, despite this handicap, soybean oil can be chemically treated, *i.e.,* reacted with fumaric acid or maleic anhydride, then esterified with a polyol. This treatment allows it to compete favorably with other drying oils on a cost-drying basis.

Safflower Oil

Safflower oil is the newest addition to the ever-increasing inventory of the printing-vehicle manfacturer. Although the merits of safflower oil are well known, it might be well to expound on those properties of particular benefit to the printing-ink industry.

Although the iodine number of safflower oil is considerably lower than that of linseed, it has been our experience that the difference is not proportionally reflected in the heat-bodying and drying rates of the respective oils. Properly formulated safflower-oil vehicles can in many instances serve as a direct replacement for linseed-oil vehicles. While nonyellowing vehicles are not as important in the ink field as they are in the coating field, they are important in certain ink applications, tin printing, for example. In these particular instances safflower oil can be used to definite advantage to obtain nonyellowing white inks.

Driers and Drying Oils

A word about driers and drying oils seem appropriate at this time. All printing inks which are formulated with drying oils, be they modified with resin or not, invariably contain driers to hasten the speed of set. This is necessary because of the many factors which can adversely affect the drying of oxidizing printing inks. Consideration of the fact that printed sheets are usually stacked in piles and further consideration of the fact that little air (oxygen) reaches the innermost confines of the pile, the importance of driers and quick-setting vehicles can be fully appreciated.

The type of stock influences the choice of drier. Stocks that are hard and highly finished require inks made with hard-drying oils, and they should contain a good percentage of strong drier. In contrast to this, highly absorbent stocks require less drier.

Other factors, which come to bear in an adverse manner upon the drying of oxidizing oil inks, are relative humidity and moisture content of the stock. Where high humidity or high moisture content of stock is encountered, fast-drying oils and/or strong driers are required.

Oil Resin-Systems

As mentioned earlier, ink vehicles today seldom consist of 100% oil. Rather the oil is combined with resin or reacted with other chemicals, as in oil-modified alkyds.

Oleoresinous vehicles constitute a very important segment of drying-oil coatings. Although oils in themselves furnish excellent ink vehicles, specifications set by printer and customer more often than not require the use of oil-resin combinations to meet their demands. As illustration, carton printers emphasize the need for hard, nonscuff type of films. The abuse which a printed carton must withstand is of a high order. They must not only resist the abrasive action of fast-moving belts used on automatic filling and gluing machines but must also be able to withstand the rubbing action that takes place between filled cartons during the shipment. The need for tough, hard ink films is thus apparent. Resin-oil combinations meet this need in handy fashion.

In general, resins contribute gloss and hardness and speed the rate of dry of oil-based varnishes. Here again the type of resin can materially affect the drying rate; pure phenolics speed up drying the most; modified phenolics are a close second; and at the end of the drying scale are straight rosins.

Most regular ink varnishes belonging to the oleoresinous system are 100% solids. If volatile solvents are used, they constitute only a small fraction of the batch. However certain ink formulations require the presence of larger percentages of volatile solvents in order to meet faster drying schedules. When the solvent type of inks are properly formulated, the solvent quickly leaves the printed ink film primarily by selective diffusion into the stock. Some evaporation from the ink surface does, of course, occur.

Gloss-producing inks are almost always a customer demand, and the use of oils is one sure way to obtain good gloss. In cooking oxidizing oils with resin, we have experienced the best gloss results when we matched resin solubility with oil viscosity. Resins which are of a high melting-point and are in the poorly soluble class furnish the best gloss-producing inks with high-viscosity oil. Easily soluble resins generally give the best gloss results when combined with oils of low viscosity.

Oil-Modified Alkyds

Oil-modified alkyds have been used with considerable success in printing inks. The advantages experienced by the paint industry in using alkyds are similarly known to the ink industry. Cost is often a more critical factor in formulating inks hence alkyds are somewhat more restricted in use in our field of endeavor. Again, where cost is a factor, good results from a product-and-cost standpoint have been obtained by using tall oil as the oxidizing portion of the vehicle.

Perhaps no one group of the ink industry exhibits a greater concern or shows a larger interest in alkyds than those who are associated with metal decorating. Alkyds are becoming, if they have not already become, the backbone of the tin-printing industry.

One of the trickier aspects of alkyd formulations is to undertake development of a tin-printing alkyd for not only is such a vehicle expected to dry faster, harder, and with less discoloration than a normal oleoresinous vehicle, it is also expected to resist the "triple threat" of offset printing: scumming, piling, and stripping.

In formulating a tin-printing alkyd, the oil portion of the alkyd is almost indispensable because it provides for what hydrocarbon solubility the alkyd possesses and also adds to the good flow-characteristics of the finished ink.

The importance of good flow and spreading on a tin panel can be more fully appreciated if one realizes that excellent ink coverage is expected in offset printing with unbelievably thin films of ink. Offset printing often deposits ink films in the neighborhood of .0001 in.

Over-Print Varnishes

O.P. varnishes find themselves occupying a larger and larger niche in the over-all scheme of printing-ink vehicles. O.P. varnishes serve a very definite function, a function which is dual in nature. Such products as catalogs, magazines, cartons, etc., which are handled considerably and are subject to soiling can be protected by the application of an O.P. varnish. At the same time these products are made more attractive by the increased luster and brilliance imparted to them by the over-printing process. True the printer would like to obtain these results with straight inks but often, to gain specific results he desires such as fast dry, toughness, and flexibility, he must formulate so as to suffer loss of gloss.

Over-print varnishes are complicated mixtures containing drying oils, resins, waxes, solvents, driers, greasy lubricants, and sometimes corn starch. Initial color and color retention should be given uppermost consideration when one attempts to formulate an oil-based O.P. varnish.

Oils are selected on the basis of their color-retaining properties, speed of dry, hardness, gloss, and scuff-resistance qualities. The resins used are selected for similar reasons, but in addition to these properties they must possess good solubility and wetting characteristics.

One other point of prime importance concerns varnish hold-out, that is, the ability of the printed and dried varnish to sit up high and glossy on the stock. Hold-out is a necessary and vital property for O.P. varnishes; without it you have no O.P. varnish. To achieve this, oil and resin must be so formulated or so cooked that the oil-resin combination yields a rather highly polymerized, viscous base. Of course, this can be carried too far and the O.P. base can be overpolymerized. In this case the solvent-thinned base will generally behave all right on low-speed presses but not high-speed presses. When an accident occurs on the latter, an umbrella and raincoat become standard equipment for the pressman because these overpolymerized, overcooked varnishes fly off the press faster than one can run for protection, and, in no time at all, everything in sight is coated with a heavy layer of varnish. If one is lucky, some varnish might be found on the stock.

What of the future? What type of oil vehicles will the printing-ink people need? As you can see, we need tough, scratch-resistant vehicles, fast-drying on the substrate but nondrying on the rollers of a press. Reduction of odor upon drying is another area where drying oils should be improved. These are just two areas that need improvement, and with constant work I am sure we shall see improvements brought about by cooperation of the printing ink manufacturers with the producers of drying oils.

Drying Oils in Floor Coverings

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In order to provide some background and perspective for discussion of the position of drying oils in resilient smooth-surface floor coverings, it may be helpful to review briefly the types of products, their relative production, and their use of raw materials. Resilient smooth-surface floor coverings may be arbitrarily divided into two categories, sheet goods and tile. Sheet goods are produced in rolls up to 90 ft. long and from 6 to 12 ft. wide. Tiles are produced, of course, in the familiar 9 x 9 in. and other sizes. Sheet goods may be subdivided into two categories, those based on drying oils, which are linoleum and felt base, and those based on resins of polyvinyl chloride and its copolymers. Linoleum is characterized by a wearing surface, up to ⅛-in. in thickness, in which the color and pattern are carried through to the backing. Felt base consists of a heavy coat of enamel paint, up to 6 mils thick, on a saturated felt backing. The service lives of the two products are proportional to the thickness of the wearing surface. Floorings based on polyvinyl chloride are similar in many properties to their drying oil counterparts; the principal difference, of course, is in the binder, which is a synthetic resin. In the "sheet vinyl" flooring the wearing surface is relatively thick, and the design is carried through to the backing. Synthetic resin counterparts of printed felt base are also available, where the vehicle is based on polyvinyl chloride and other resins instead of drying oils.

In the field of resilient tiles there is the familiar asphalt tile, based on binders having a bituminous derivation. Additional types are cork tile, rubber tile, linoleum tile, and tile based on resins of polyvinyl chloride and its copolymers.

The technology of resilient floor coverings has been described previously in the Journal of the American Oil Chemists' Society (1). There is also a very good article on the technology of floor coverings in the Encyclopedia of Chemical Technology by Kirk and Othmer under the subject of "Linoleum" (2). Generally speaking, all of these types are prepared from a drying oil or resinous binder, to which are added fillers and pigments to form a somewhat thermoplastic mix. This mix then is formed into flat sheets of various sizes by a variety of methods to produce either sheet goods or tile.

It would be appropriate now to discuss the statistics of the industry so as to provide some idea of the importance of each of these types of floor coverings and the usage of raw materials in each one. These statistics are accumulated by various branches of the federal government and are available in fairly good form up through about 1955. Since then there has been a distinct shrinkage in the number of producers so that