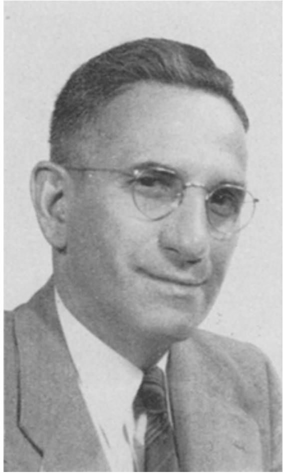
Drying Oils in Printing Inks

I. M. BERNSTEIN, Gotham Ink and Color Company,
Long Island City, New York

Introduction

THE use of drying oils in printing inks dates back to the earliest periods of recorded history, following that of carving on stone. Some of the earlier applications were those of the ancient Chinese and the religious block prints made during the middle ages. The close identification of the natural drying oils with printing inks followed as a consequence of the fact that, with the exception of Japanese lacquer, these oils constituted practically the sole method known at the time for achieving film formation. This situation persisted essentially unchanged through the centuries until relatively recent times. For inks which have to dry hard on relatively non-absorbent paper and other surfaces, and this includes practically everything except newsprint, the drying oil type continued until roughly 1925 to dominate the printing ink industry. Newspaper inks, which dry by absorption and penetration, are of course in a different category since their vehicles are non-film forming.


I. M. Bernstein

Economic Analysis of Consumption

During the past 25 years, as a consequence of the great strides resulting from research, many newer and faster methods of accomplishing film formation have become available (1). Today film formation in printing inks is keyed increasingly to the new tempo requiring split second drying. This is particularly true of the national circulation magazines, and to a smaller but ever increasing extent of printing for food packaging. As a consequence of this trend the use of drying oils for inks in these important volume fields has been considerably reduced. Drying oils, whether conjugated or non-conjugated, are commercially not capable of such rapid film formation by the conventional process of oxidation. The progressive decline in the use of these oils by the printing ink industry appears certain to continue. This is, of course, not to say that the drying oils are not still very important vehicles in this field or that they do not still constitute a large volume, but the fact must be faced that the present trend away from them is a definite one. How far this trend will go before leveling off is difficult to predict. To a very great extent it depends on future scientific and technical developments in the drying oil field itself as well as on the economics involved.

It is interesting and instructive to follow this trend through the years, 1932 to 1949. This will be done using the data given in Table I, furnished by the U. S. Department of Commerce. In this table data are also given of the comparative situation in the paint and varnish field (roughly 10 times the size that of printing inks) to illustrate certain economic factors.

TABLE I

Total Consumption Primary Animal and Vegetable Fats and Oils

Year	Used in Printing Ink (1,000 lb.)	Printing Ink Dollar Sales	Used in Paint and Varnish (1,000 lb.)	Paint and Varnish Dollar Sales
1932	10,431		254,243	
1933	13,419	26,166,304	297,560	220,303,894
1934	15,544		329,894	
1935	18,000	34,534,951	394,005	334,277,609
1936	20,206		428,668	
1937	26,213	47,346,545	458,522	402,126,113
1938	21,884		358,134	
1939	22,873	43,600,000	425,113	379,276,938
1940	21,178		434,736	
1941	29,319		570,802	
1942	....		....	
1943	22,498		444,342	
1944	30,036		536,156	
1945	37,331		475,562	
1946	33,095		502,840	
1947	23,098	109,901,000	589,683	1,053,995,760
1948	21,740		591,290	

The year 1932 was the depth of the depression hence the low consumption of roughly 10 million pounds by the printing ink industry. By 1937 the economic situation was definitely on the mend, with the consumption increasing to 27 million pounds. The years 1938 through 1940 represented a slight recession with a corresponding lowered consumption. For the years 1933, 1935, and 1937 the annual dollar sales followed quite closely, either up or down, in the same ratio as drying oil consumption, indicating that the ink industry was still primarily dependent on these products for film formation and that the faster methods of printing demanding different vehicles had not as yet reached significant proportions. By comparison the paint and varnish industry which has its own particular trend away from drying oil consumption, utilizing to a greater extent the alkyds, lacquers, and water emulsion vehicles, showed in these years about a 15 to 20% increase in dollar sales in excess of its increased oil consumption. The country had pulled out of the recession by 1940 with a then all-time high for the ink industry of over 29 million pounds, when the war struck. During 1942 and 1943 wartime quota restrictions dropped the consumption considerably, but their lifting in 1945 for printing inks raised the consumption level to an all-time high of over 37 million pounds. After the war's end came the period of inflationary bidding for the relatively low stock of domestic oil then available since the normally high Argentine supply was in economic and political dislocation. This trend was noticeable also in the paint and varnish industry but with this difference that, whereas for paint and varnishes the drying oil consumption rebounded by 1948 to an all-time high of over a billion pounds, consumption for printing inks receded in this year to the 1938-1940 level of about 22 million pounds.

This situation was not the result of low business activity in the printing ink industry. To the contrary in 1947 the dollar sales had reached 110 million dollars, an increase of 150% over that for 1939, and this has increased since even more without any increase in drying oil consumption. The paint and varnish industry in the same 1939-1947 period also experienced an increase in dollar sales of 160% but with this difference, in contrast to the backward trend of oil consumption for the ink industry to the 1939 level that for paint and varnishes rose about 40%. We can therefore see quite clearly for the first time the effect of substitution of other film formers for the drying oils, particularly in the printing ink industry. As has already been stated, this substitution was not the reflection of a passing price differential period but was due in large measure to the inexorable economic demand of the publishing industry for printing inks which would dry instantly.

The Speed Problem

One may well pose the question, is it not theoretically possible to accelerate the rate of oxidation of drying oil films so as to compete with the evaporation and phase displacement methods of film formation which have paced the way in this trend? The difficulty of the problem lies in the necessity for accomplishing the oxidative film-forming process commercially in say a tenth of a second, the time allotted in high speed magazine printing, operating for example, at a web speed of at least 1,200 feet per minute. The conventional approaches to the problem have been tried, those of conjugated oil systems and the use of peroxide catalysts, but these have not been found satisfactory, aside from the high costs involved. This is not to say that the problem cannot be solved but rather that the age-old concepts of oil drying must be revised and revitalized before a solution can be effected. The principal difficulty appears to be that the fundamental scientific aspects of the mechanism of the film-forming process of drying oil systems have hardly begun to be studied. The recent work reported by Long (2) and Bowles (3) on film formation are steps in the right direction. In this connection the styrenated alkyds which, while not generally adaptable at present to printing ink formulations, at least show some possibilities in this direction. The theory involved will be discussed later in the paper.

The Odor Problem

Odor is another major factor in today's printing ink requirements, of prime importance in the food packaging industry. The tremendous strides which have been made in food packaging in the past 15 years have indeed constituted a revolution. To go into a modern market is to enter an inkmaster's paradise. Brightly color-printed packages made of metal, paper, parchment, foil, glassine, cellophane, vinylidene chloride polymer, pliofilm, and polyethylene vie with one another to catch the customer's eye. Suppose in such a competitive scheme one of the packages had an unpleasant odor caused by the printing ink used. Consumer reaction against it would certainly be prompt and definite. In drying oil inks there are two types of odor, one the initial odor of the materials used, and two the odor of the acidic and aldehydic oxidation decomposition products resulting from the drying process. The latter in particular is a constant source of concern to the printing ink manufacturer and to the printer. In contrast to this, with the evaporation and phase displacement type of inks such as a gravure, aniline, steam set, and heat set, assuming proper selection of solvents and binders, the odor problem vanishes in thin air and accounts in part at least for the trend in their direction.

Notwithstanding this, there are still great areas of the printing industry, such as for example the fast growing field of offset lithography, which are still dependent in large measure on inks using drying oil vehicles. In these fields speed and odor have not as yet become critically involved. Let us therefore examine in some detail the drying oil field, both natural and synthetic, with respect to the printing ink industry for an understanding of the requirements and difficulties involved.

The Natural Drying Oils

The traditional and still dominant vehicle of printing inks is heat-bodied linseed oil. This, as is well known, is made in the age-old manner by heating the oil in a metal kettle, open or closed, to about 585°F. and holding the oil at this temperature until any of several viscosities from 3 to 600 poises is obtained. These vehicles have excellent pigment wetting and pigment dispersion characteristics, dry well though not rapidly, and possess quite good adhesion. The drawbacks are relatively poor alkali and soap resistance and somewhat limited flexibility. There is considerable difference in the important flow property of an ink, depending on the heating history of the linseed vehicle used. Good flow is a unique and necessary property in printing inks since without it an ink cannot be uniformly distributed on a press. This property was studied in considerable detail some years ago by the late J. J. Mattiello (4). In general the heat-bodied linseed oils are such good vehicles that until about 15 or 20 years ago there was little incentive to change them or even to understand the basic mechanism of their formation. To date some progress has been made. It is interesting to note how linseed has dominated the use of drying oils in the ink field through the years. This information is given in Table II, compiled from data furnished by the U. S. Department of Commerce.

TABLE II

Percentage Consumption of Primary Animal and Vegetable Fats and Oils by the Printing Ink Industry

Year	% Linseed Oil	% China Wood Oil	% Perilla Oil	% Soybean Oil	% Remaining Oils, Greases, Wool Grease
1932	87.5	6.7	1.9	......	3.9
1933	81.3	11.2	3.0	......	4.5
1934	81.3	10.9	3.9	......	3.9
1935	79.5	11.1	4.4	......	5.0
1936	74.2	11.4	9.9	......	4.5
1937	77.5	10.7	6.9	......	4.9
1938	76.7	9.5	8.2	......	5.6
1939	76.4	9.2	8.2	......	6.2
1940	80.7	8.0	5.2	......	6.1
1941	80.2	10.2	2.7	......	6.9
1942	......	......	......	......	......
1943	95.1	......	......	......	4.9
1944	91.6	0.7*	......	......	7.7
1945	91.2	1.7*	......	......	7.1
1946	91.8	3.0*	......	0.3	4.9
1947	83.5	6.7*	......	4.8	5.0
1948	84.8	6.9	......	1.0	7.3

* Includes oiticica oil.

From Table II it is also evident that aside from china wood oil, which has a special place in printing ink formulation, the only threat to linseed was perilla oil which rose to a maximum consumption of 9.9% in 1936. Perilla oil is a particularly fine oil for use with modified phenolic resins in the making of gloss inks and for the making of tough, hard-drying alkyds for use in metal decorating inks. In addition, perilla oil heat bodies like linseed and is an excellent grinding vehicle. It unfortunately dropped out of the picture during the early years of the war and, since it is produced solely in Soviet-dominated Manchuria, has not been marketed in the United States since.

The only other oil which has had a steady and sizable place in printing inks is china wood oil. Previous to World War II it averaged about 10% of the drying oil consumption and was used chiefly in overprint gloss varnishes for enhancing the appearance of label and carton printing and for soap wrapper ink vehicles in conjunction with phenolic resins. During the war its use was generally severely restricted and not allowed at all for printing ink consumption. After the war its use slowly came back and by 1948 amounted to about 7% of the total drying oils. One may well ask how china wood oil can be used in printing inks in view of its pungent odor. While the initial odor of this oil is strongly characteristic, it absorbs roughly about 3% of oxygen on drying in contrast with about 25% for linseed oil. The odorous oxidation decomposition products from china wood oil are therefore proportionally less.

With regard to soybean oil, in only one year did its use achieve significance, 5% in 1947. By itself soybean oil bodies slowly although it can, given time, go through all the stages of heat polymerization including that of gelation. While the upgrading and segregation techniques in recent years have to a large extent eliminated its low functionality, the enormous demand for soybean in the edible field has practically eliminated it from serious consideration as a drying oil, either for printing inks or paints and varnishes. Moreover the price incentive, which was very much in its favor as against linseed in the early post war years, is now in the process of stabilization with the return of linseed oil to successive lower price levels.

The other drying oils, principally fish and dehydrated castor, are indeed only slightly used in the printing ink field since all these, together with animal greases and wool grease, amount to only about 5%. Tall oil is also used but in relatively small quantities.

Although the percentage use of linseed oil has remained substantially constant through the years, this must not be taken to mean that its use is as restricted today to the production of the heat-bodied vehicles as was previously the case. Within the past 20 years and more particularly within the past 10 years, there has been an increased interest in special types or forms of linseed as well as of other drying oils. This expansion towards modified or synthetic oils will now be discussed with the object in mind of indicating vehicle trends in the printing ink industry.

The Synthetic Drying Oils

The first of these modifications was the long oil 100% alkyd which came into favor about 1935. These alkyds are excellent grinding vehicles, giving inks which have good flow characteristics at high pigment loading. Furthermore, alkyd inks dry relatively fast and hard and have excellent adhesion and flexibility. Although the prices of the alkyds are high, their generally excellent qualities have resulted in their being used in increasing volume, particularly in metal decorating lithographic offset inks. They are also used in high grade coated paper inks for printing both by letterpress and offset lithography. As is well known, various modifications of the alkyds have been proposed and marketed. In general, the best alkyds for printing ink use are the phthalate linseed type although these were surpassed in the years preceding the war by the perilla alkyds.

After the introduction of the alkyds there was a rather long period in the ink industry in which there was little of a new or novel nature in vehicles. The prime incentive to the considerable work which was done in the upgrading of linseed and other oils by the paint and varnish as well as by the printing ink industries during the past 10 years had its inception in the withdrawal of china wood and perilla oils and the severe restrictions placed on the alkyds following our entry into World War II. This work centered at first on the utilization of the then recently introduced polyalcohols such as pentaerythritol, polypentaerythritol, and sorbitol as a means of increasing the functionality as well as the monomer size of re-esterified unsaturated drying oil acids. From a printing ink point of view such synthetic oils are quite useful in increasing drying speed and alkali resistance, but they unfortunately have rather limited synthetic resin compatibility in the high melting point range, which defect together with their high price tends to restrict their general acceptance. Their increase in drying speed, for example, while a desirable quality was not, even in 1942, of the order of magnitude required for the high speed trend which was rapidly gaining momentum in the printing and publishing industry. This shortcoming was also present in some of the other methods used in the upgrading problem. It was in this respect that the requirements of the printing ink industry diverged sharply from those of the paint and varnish field which found these oils of considerable usefulness along conventional lines.

Let us examine briefly some of the other upgrading methods which are of a more chemical nature. These processes utilize chemical reaction of the natural triglyceride oils with such unsaturated compounds as maleic anhydride, styrene, and dicyclopentadiene, among others, to increase functionality and molecular complexity.

The maleinized oils were the first of this group to be offered. They have enjoyed to date generally good acceptance in the printing ink industry although the degree of upgrading in terms of increased drying speed is again only moderate. These oils have good resin compatibility in contrast to the polyalcohol types. When properly formulated, the maleinized oils make vehicles which have excellent working qualities for offset lithographic inks; that is, they wet and disperse pigments well, allow high pigment loading while maintaining good ink flow, and resist the acidified water etch solution which is an integral part of the lithographic printing process.

The styrenated oils, or more properly styrene reacted natural drying oils, came into the picture shortly after the war's cessation, as a consequence of the availability of excess styrene from the synthetic rubber program. Their principal defect is that while they disperse pigments very well, the resulting inks are of a short body and hence do not possess the required flow characteristics for good press performance. Styrenated oil inks dry quite rapidly and hard, better in this respect than heat-bodied linseed oil or linseed alkyds. In addition, they possess excellent soap and alkali resistance. By and large however they have not enjoyed more than a mild vogue. The styrenated alkyds which are another phase of this same development will be discussed later.

The third of the chemically treated oils to venture into the printing ink field were the dicyclopentadiene oils. These again are more properly designated dicyclopentadiene reacted natural drying oils. The dicyclopentadiene oils heat-body well, dry faster and harder than the parent natural oils, and have quite outstanding resin compatibility. Their chief defect lies in their rather poor pigment wetting and dispersion characteristics. This is particularly the case with carbon blacks and unresinated organic colors. At the present time there is considerable interest in the fish oil type of this product because of its low cost compared to linseed. How long this decided price advantage of several cents a pound will remain is difficult to say in view of the progressive return of linseed oil to a more competitive position. If the dicyclopentadiene oils are to increase or even maintain the toe-hold they have obtained in the printing ink field, it will be necessary to solve the pigment dispersion problem. At the present time the dicyclopentadiene fish oils maintain their interest principally on price, a somewhat tenuous hold in a field where in the long run quality is of prime importance. If, on the other hand, the pigment wetting problem can be solved, then the normal price differential in favor of fish oil should give this type of dicyclopentadiene adduct a definitely favorable position not only in printing inks but also in paint and varnishes. With regard to the characteristic initial odor of fish oils, this has been minimized in the dicyclopentadiene adducts although certainly not eliminated. This factor will therefore also be present in the final economic assessment of these oils for use in inks.

Still another type of synthetic product is the so-called petroleum drying oil. In the immediate post-war years there was a good deal of interest by printing ink manufacturers in one type of this material, primarily because of its very low price. These oils essentially are highly unsaturated resins, obtained from petroleum cracking, which are then dissolved in approximately 50% of more or less saturated petroleum solvents of moderately low volatility, and so marketed. The earlier products had a very pungent and objectionable odor and were quite dark in color, but these defects have been minimized in more recent offerings. The oils have excellent pigment wetting and dispersion characteristics and dry even better than linseed. The dry films are, as one would expect in view of their resinous character, quite brittle and to a surprising extent hydrophilic. This is not too great an objection for many printing ink uses although it is nevertheless a defect. Because of their high iodine value, roughly 220 Wijs, the oxidation decomposition odor is also a factor to be considered. At the present price level of the refined grade it is somewhat questionable, in view of the price-wise return of linseed oil, whether further expansion will occur in the use of the petroleum drying oils by the printing ink industry or indeed whether they will even retain their present sales position. This is not true of course of the crude highly odorous oils which are quite cheap, but these in their original form cannot be used in quality printing inks.

This brings us to a discussion of the styrenated alkyds, which are of great potential interest to printing ink manufacturers although as yet the interest is not too active commercially. The same applies to the drying esters obtained from resinous polymeric alcohols of the bisphenol-epichlorhydrin type. Because the latter are not commercially available to the printing ink industry at the present time, the discussion will be limited to the styrenated alkyds.

These alkyds have one really outstanding property, that of almost immediate drying even without metal catalysts, in the thin films typical of printing ink application. Such instantaneous film formation is not due to solvent evaporation since normal alkyds of comparable oil length and solvent content do not exhibit this phenomenon but air dry in the conventional manner. Certainly it cannot be due to the normal process of oxidation and/or polymerization since the time interval is entirely too short. This leads to the interesting inference that film formation in drying oil systems may be primarily a combined orientation and gelation process, usually initiated by the product or products of oxidation, but in the general case not dependent upon them. Furthermore it is customary to consider the dry films are being more or less irreversible, but again this is not necessarily true. We know, for instance, that normal phthalate alkyds when air dried are quite thermoplastic at elevated temperature, much more so than oxidized triglyceride oil films even though the drying rate of the alkyds is faster. The extent and type of cross-linkage appear to be the determining factors with respect to the rigidity and reversibility of the system. Some general comment will be made now regarding the reversibility factor in dry films and of film formation itself, from the point of view of the forces involved, as an aid to the better understanding of the styrenated alkyds.

Concepts of Film Reversibility

Three types of reversibility may be considered, a) that involving primary chemical bonds, b) that involving both primary and secondary bonds, and c) that involving secondary bonds alone.

Examples of the first are the insoluble infusible cross linked polymers present in and recently isolated from heat polymerized drying oil gels (5), and similar polymers in high baked oxidized finishes. Here a considerable degree of conversion to three dimensional polymers has taken place on the basis of primary or covalent bond formation which has of course maximum irreversibility.

As an example of the second let us consider ordinary temperature oxidation drying. The primary bond oxidation reaction takes place first, producing the proper structural units. This is then followed by orientation and secondary or Van der Waal bonding to form the gel or film. It is the primary bond oxidation reaction which accounts for the long inductive period typical of this type of drying. Once these structural units are present the onset of film formation is quite rapid. The molecules or micelles have to approach each other only to the extent of 3 to 5 Angstroms for secondary bonding instead of the 1.54 Angstroms in primary C-C bonding with its concomitant high repulsive forces and high energy activation barrier (6). This secondary bond type has intermediate reversibility depending on the temperature and may even exhibit syneresis, as in the development of after-tack.

This brings us to the third type in which the structural units do not have to be pre-formed but are the system itself. Here cross linkage and rapid film formation is due solely to secondary valence bonding. Two cases may be considered, a) where the secondary bonding is weak, 500 calories, and b) where it is strong, 5,000 calories per atom or atom group. With respect to the first I prepared some years ago pseudo oil ink films which dried to touch in a moment or two but were repeatedly reversible to the sol stage merely by agitation at room temperature (7). In these films the secondary valence bonding is of course quite weak. The styrenated alkyds which belong to the second type also undergo film formation promptly in accordance with the facile orientation and secondary bonding of the inherent structural units of the system. The secondary bonding is quite strong, and the films have a considerable degree of irreversibility at ordinary temperatures. Of course being a drying oil system, the styrenated alkyds subsequently continue to oxidize and harden further.

As is quite apparent the split second film formation obtained with the styrenated alkyds brings the drying oils for the first time within the scope of the high speed printing operations previously discussed. From this point on it becomes an economic question as to whether this new approach to drying oil film formation can compete in price and qualities with the currently used rapid methods of evaporation and phase displacement. The styrenated alkyds now on the market require aromatic solvents as the thinner which limits their use to gravure printing. Another limitation is their rather strong odor, caused by unreacted styrene monomer, which is a decided drawback in the food packaging field. The odor will have to be eliminated before serious commercial consideration can be given to this interesting material. Notwithstanding their present limitations, the styrenated alkyds and other drying oil adducts which film-form by a similar mechanism offer one possibility as to the way out of the present dilemma of the drying oils in the printing ink industry.

Conclusion

An analysis has been made of the historical position of the drying oils in the printing ink industry, of their current curtailed usage, and of the performance requirements of drying speed and minimized odor which have contributed to this curtailment. The situation from the long-range viewpoint is a serious one. It is a challenge and opportunity alike for the oil chemist to understand in a fundamental sense the physics and chemistry to the process of film formation of the drying oils. The styrenated alkyds and the bisphenol-epichlorhydrin esters point the way to the concept of film formation of drying oil systems in which oxidation is not the dominant factor.

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Miscellaneous Uses of Drying Oils

S. S. GUTKIN, Falk and Company, Pittsburgh, Pennsylvania

OILS consumed under the categorical heading of "miscellaneous uses" have been growing in considerable volume. The Bureau of Census reported 93,000,000 pounds consumed in 1943; this quantity increased steadily to 180,000,000 pounds in 1948. These miscellaneous uses of drying oils are diversified and cover a wide latitude of application. Grouped in this classification are all the end uses of drying oils not covered by paints, varnishes, resins, linoleum, and printing inks. The facets of the uses are so numerous that a paper such as this must of necessity, be limited. Generally, miscellaneous uses cover all the oil consumed in putty, mastic, caulking and deadening compounds, insulating material, rubber, rubber-like compounds and coated fabrics, core oils, stamping and drawing compounds, rustproofing agents, slushing and metal tempering oil, binders for brake blocks and fibre gaskets, stiffening agents for pressed wood hardboard operations, petroleum additives for pneumatic tool and steel cylinder stock lubricants, fluxes for tin and terne plate, textile sizes, roofing compounds, leather treatment, wood treating chemicals; pharmaceuticals, toilet articles, disinfectants, detergents, insecticides, fungicides, etc. Most of those enumerated above will be treated to a lesser or greater degree in this paper as the demand may require or the information covering is available.

S. S. Gutkin

Caulking Compounds. Of all the miscellaneous uses of drying oils those used in the manufacture of putty, glazing, and caulking compounds are familiar to coating manufacturers to about the same degree as paints. There is a relation between caulking, glazing compounds, and putties, since all are "over-pigmented vehicle plastic bases" and may in many cases be used interchangeably.

The function of caulking compounds is to fill joints between wood and wood, wood and masonry, metal and masonry, or between masonry and masonry. Caulking compounds are available in three grades, gun grade, knife grade, and cord. Sometimes the last type is