DEPARTMENT OF COMMERCE

# CIRCULAR

OF THE

# BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 53

# THE COMPOSITION, PROPERTIES, AND TESTING OF PRINTING INKS

[1st Edition]
Issued March 29, 1915

WASHINGTON
GOVERNMENT PRINTING OFFICE
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# THE COMPOSITION, PROPERTIES, AND TESTING OF PRINTING INKS

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## INTRODUCTION

This circular contains an account of the nature and properties of printing inks and of the materials used in their manufacture. It includes, in addition, a brief reference to the methods employed at this Bureau in the analysis of printing inks. Those who wish a more complete description of the analytical methods are referred to the separate publication on this subject.[1]

## HISTORICAL

It is natural to think that printing inks should date back to the first printing press. In so doing we forget that to the Chinese many of our modern discoveries are very old stories.

It seems quite certain that as early as 50 B. C. a rather primitive method of printing was known to this people. It can readily be imagined that advances in the art of printing were rather difficult, for in this language each word requires a separate character and a job printer would require something over 15 000 characters to meet only the very ordinary demands of his work. However, as early as 927 A. D. certain volumes were printed from stone blocks for the Imperial College at Peking. In the printing of these books the characters were cut into the surface of the stone, so that when printed they appeared white on a black background. Shortly after, engraved blocks of wood were used on which the characters were raised, and the printed page appeared with black characters on a white paper. For ink the Chinese had at their disposal a very satisfactory black pigment which they had been using for writing purposes, the manufacture and properties of which were well known to them. It was necessary merely to mix this with an oil to get a fairly satisfactory printing ink.

In Europe printing as an art became quite general during the early part of the sixteenth century. Many specimens of this early work exist in the various museums and are of great interest. In some cases the ink has remained an intense black, with no sign of fading. This is no more than would be expected, for the pigment in these inks is principally carbon, one of the most stable pigments known. It may be accepted, however, as a general proposition, that the life of a printed page depends not upon the lampblack but upon the durability of the paper and of the oil which binds them together. In some of these early books, owing either to impure lampblack or inferior or improperly prepared oil, the printing has offset on the opposite page, a fault which occurs in books of modern times.

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[1] Bureau of Standards Technologic Paper No. 39, "Analysis of Printing Inks," by J. B. Tuttle and W. H. Smith.

The early printer usually made his own ink, and the literature contains many stories of how the staff of the early printing shops would occasionally take a picnic in the fields, set up their kettles, and proceed to boil linseed oil, the festival culminating in a feast of bread which had been toasted in the hot oil. It would not be at all surprising if this early custom was responsible for the idea that bread made a good "oil drier," and was probably first established by a printer who found that on the day he had made a good varnish some of his apprentices had accidentally dropped their bread in the oil.

This scheme for making ink was not satisfactory. Too much time was lost and the ink did not always turn out well, so that by the seventeenth century it was quite common for the printer to buy his inks ready-made. That dishonesty, or ignorance in manufacture, is by no means confined to recent times is quite evident from the statement of Moxon, in his "Mechanik Exercises" (1683), when he says:

> The providing of a good inck, or rather a good varnish for inck, is none of the least incumbent cares upon our master-printer, though custom has almost made it so here in England; for the process of making inck being as both laborious to the body, as noysom and ungrateful to the sence, and by several odd accidents dangerous of firing the place it is made in, our English master-printers do generally discharge themselves of that trouble; and instead of having good inck, content themselves that they pay an inck maker for good inck, which may yet be better or worse according to the conscience of the inck maker.[2]

The history of ink making shows that the development of the industry followed the improvement of inks, to gain the desired consistency, along the following lines: First, the ink must have a certain body; second, it must have a certain cohesion, or flow (long or short); and third, a certain adhesion or tack. An ink or varnish is "long" when a drop falls away from a spatula with a long hairy string or thread; it is "short" when the drop is cut off sharply, with a very small tail.

There was considerable difference between the methods of the early English and Dutch ink makers. The latter used only linseed oil, with a small amount of added rosin, whereas the English added a considerable quantity of rosin, and even mineral oil, to an insufficiently boiled linseed oil.

The early varnishes[3] were almost invariably made by heating the oil to the point where the vapors would take fire (a red-hot poker was supposed to have special advantages in starting the burning), testing the burning oil

[2] Inks, their Composition and Manufacture, by Mitchell and Hepworth, p. 136.

[3] Varnish, as used in the printing ink trade, has two general meanings—first, linseed oil which has been heated at or near its flash point, with or without permitting it to take fire; and second, the whole body of all the vehicles, or media which carry the pigments, even including the driers.

from time to time, and stopping the process when the cooled sample showed that it had attained the desired consistency. The kettle was then covered, and when the oil was cold it was mixed with smoke black or lampblack, and the whole mass ground together with the old-fashioned muller stones. This process is in use to-day in the preparation of varnish for plate inks.

The latter part of the eighteenth century developed the use of litharge in boiling the oil, but it did not receive universal commendation and was soon abandoned. The principal objection was that a varnish prepared with litharge clogged the type. The early part of the nineteenth century saw the introduction of soap, to make the ink leave a clean, sharp impression on the paper and to prevent the clogging of the type. It had the further advantage of thickening the ink, so that the oil did not have to be boiled, or burned, as long as would otherwise have been necessary.

In 1823 Savage, who had studied the manufacture of printing ink from the point of view of the practical printer, published a book in which he discussed the various methods of manufacture. His recommendation of old linseed oil brings forward an idea which has since received considerable attention from ink makers, viz, that the oil used for printing ink must be carefully purified. An old oil would, of course, be comparatively free from foots or sediment. In case such an oil is not available, mechanical means must be employed to clarify the fresh oils.

The eighteenth century developed the idea of adding a blue coloring matter to neutralize the yellow of the oil, using for this purpose Prussian blue and indigo. The nineteenth century saw the development of the aniline dye industry, following the synthesis, by Perkin, of mauve, the first aniline color.

Meanwhile, owing to a desire to reduce the cost of inks as well as to secure inks which would work better on the various grades of paper now being made, new oils were being introduced into the ink vehicles. First of all came the introduction of rosin and rosin oil, followed by mineral oil, the long gilsonites (the latter furnishing both vehicle and pigment), the semidrying oils, and the new drying oils such as China or tung oil, etc.

We thus arrive at the twentieth century, and find the materials for making printing inks pretty thoroughly studied, and in general very much what they were in the beginning. Recent advances have been along the line of mechanical devices for the manufacture of large quantities at a minimum of cost. So far as materials are concerned the principal progress has been in the preparation of colored inks, used so effectively in the multicolored lithographic work.

## COMPOSITION OF PRINTING INKS

### CLASSES OF INK

It has been stated that the inks of to-day have for their foundation practically the same materials which have been used since printing ink was first made. The perfecting of the art of making paper, together with the development of rapid-printing presses, have brought into use several rather distinctive types of ink. They may be divided into two classes—first, in which the paper is fed into the press in a continuous sheet, and second, in which the paper is fed in one sheet at a time. The newspaper is perhaps the best known example of the former; the latter includes a variety of materials, such as books, cards, illustrations, etc. The composition and consistency of each of these classes of ink will depend not only upon the class of work for which they are intended—i. e., the grade of paper to be used—but also upon the speed at which the presses are run and the temperature and humidity at the time of printing. The problem of selecting the proper grade of ink is therefore far from being as simple as it might appear at first sight.

In addition to the above, there are inks for special kinds of printing, such as lithographic work and engraving, the inks of the latter class being generally known as plate inks. Investigations of these grades of ink are to be made, and the information secured will be incorporated in future editions of this circular.

Still another grade of ink is the doubletone. This consists of a black pigment, such as carbon black, and a dye dissolved in oil. It is used extensively in illustration work, calendars, catalogues, etc., where its working qualities produce very artistic results.

The Government Printing Office divides its inks into four classes—web-press, flat-bed, job, and halftone—the particular properties of each kind depending upon the paper for which it is intended as well as the press upon which it is to be used.

Web-press ink is intended for use on presses where the paper is fed in a continuous sheet or "web." These presses are run at a very high speed, reaching at times from 10 000 to 12 000 revolutions per hour. The ink fountains are of the "overshot" type, i. e., the feed roll carries the ink up and over to the distributing rolls. Web-press inks must therefore be thin, so as to feed well and penetrate the paper rapidly, and must have considerable cohesion or length, in order that there shall be no break in the supply of ink. The penetration is of particular importance, especially when the

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ink is printed on both sides of the paper practically simultaneously, in order that there shall be as little offsetting as possible. On hard papers there may be an initial penetration of part of the ink, causing it to "set," followed by drying through oxidation. With soft paper there is no drying by oxidation, and all the drying must therefore come through penetration of the paper by the ink.

In this connection it is proper to state that if inks intended to dry by absorption only are used on hard papers they will not dry rapidly, and all sorts of trouble may result. In such cases the addition of driers will not promote the drying; the remedy is to change either ink or paper.

Flat-bed ink is used in printing the better class of books, pamphlets, etc. A somewhat heavier body is required than is the case in web-press work, the ink being somewhat thicker. The drying qualities must be adjusted to the paper used, and inasmuch as the flat-bed inks are generally used on harder paper than the web-press inks the former have usually better drying qualities, i. e., drying by both absorption and oxidation. This does not necessarily mean that flat-bed inks are always superior to web-press inks; there are good and bad of both classes.

The job ink is used on platen or flat-bed presses, for printing on highly sized papers, such as bond, ledger, writing papers, cardboard, etc.

Finally, there is the halftone ink, for use in printing from halftone plates on a highly glazed or coated paper.

The flat-bed presses have "undershot" ink fountains, and are not run at anything approaching the speed of the web presses. A stiffer ink is needed, and it need not be quite so long as the web-press ink.

In order to better understand the making of ink, it would perhaps be advisable to give a brief description of the materials entering into its composition.

## OILS

Linseed Oil.—Linseed oil is contained in the seeds of the flax plant (*Linum usitatissimum*). It is very high in price, as oils go, and consequently can not be used in the cheap newspaper inks, but is unquestionably the best vehicle for the better grades. The chief virtue of this oil is that on exposure to air, in thin films, it dries rapidly to a hard surface, which adheres very firmly to the paper and is not readily affected by further exposure to light and air. Its importance is such as to warrant special notice, and in a later chapter it is proposed to deal with this material at some length, describing its manufacture and giving some of its properties.

SEMIDRYING OILS.—There are some oils, such as corn oil, rapeseed oil, etc., which possess to some extent the property of drying on exposure in thin films. These oils are called semidrying oils. They are not much used when linseed oil can be obtained at a reasonable price, but in the event that the price of linseed oil should become prohibitive, they could be used as a substitute in the medium-grade inks.

CHINESE WOOD OIL.—In recent years a new oil has appeared on the market, the Chinese wood oil, or tung oil. So far as can be ascertained this has not been used in the manufacture of printing ink, but it is not unlikely that in the course of a few years it will be used to replace part of the linseed varnish. It has excellent drying qualities.

ROSIN.—Rosin (colophony) is the solid residue remaining in the stills after the distillation of turpentine. It comes in large, irregular lumps, the color of which varies from water-white to almost black. The lighter shades are somewhat transparent, while the darker are practically opaque. The variations in color are due partly to the manner of treatment and partly to the condition of the resins gathered from the tree. It is very brittle, being easily ground into a fine powder. It is readily melted, and in this condition is added to the oil in the preparation of printing inks.

ROSIN OIL.—When rosin is subjected to distillation it yields about 85 per cent of its weight of a heavy oil, known as rosin oil. This is used extensively in inks, especially in the cheaper varieties. It is not a substitute for linseed oil and should not be used as such. When mixed with rosin and suitable driers (generally organic salts of lead and manganese) it possesses some drying properties. Its great value lies in its ability to dry rapidly by absorption, since it readily penetrates soft papers.

Rosin and rosin oil find extensive use in the manufacture of printing inks and, in their proper place, are of great value, and should not be looked upon as adulterants. The material from which an ink is made is quite unimportant, provided it has the working qualities desired, does not injure the paper, press, type, plates, etc., and is at least as permanent as the paper upon which it is printed. Furthermore, distinction must be made between inks intended for printing work which will be thrown away in a very short time (newspapers, magazines, etc.) and inks intended for more or less permanent records. It has been shown by experience that, when used as a substitute for linseed oil, rosin and rosin oil are responsible for considerable trouble, just as linseed oil has been found objectionable when it has been used to replace rosin oil in inks demanding rapid absorption. In every case it is a question of fitting the vehicle to the work for which the ink is intended.

Hard Gums.—The hard gums are the exudations from various species of tropical trees. The kinds used in printing inks are resins and not true gums; the latter term is more specifically applied to those which are soluble in water, such as gum arabic, etc., the water-insoluble gums being better known as resins. However, the collective name of hard gums is used so generally in the trade that it will be employed in this circular in preference to the more scientific name of resins.

There is little uniformity in the classification of these gums; the same name is applied in different countries to entirely different kinds of gum. Here, those known as copal, dammar, and kauri are preferred. As a class, they are hard and more or less brittle; the better grades are more or less transparent, and light in color. They fuse with difficulty, and do not readily mix with linseed varnish. This is particularly true of kauri. They are used only in special inks, where a hard glossy finish is necessary, and must be prepared with great care to produce proper results. They do not possess the same tendency to crack as ordinary rosin.

The above represent the chief constituents of the oil portion of printing inks. To a very much less extent we may find some of the heavy petroleum oils, vaseline, asphalts, or bituminous products. Sometimes other oils than linseed, having to some extent the property of drying (the so-called semidrying oils, such as corn oil, nut oil, etc.), are used in an effort to produce a cheaper ink. China-wood oil (tung oil) is the only oil which has up to the present time had any measure of success, and there is still much to be learned about it before it may be considered satisfactory. As far as the use of the semidrying oils to secure cheaper inks is concerned, it must always be considered that a certain amount of quality has been sacrificed to secure a lower price.

Soaps.—There is little uniformity in the use of soaps in the manufacture of printing inks. Some manufacturers use scarcely any, while others use considerable quantities. By soap, the metallic salts of fatty and similar organic acids is meant. This would include the common hard and soft soaps (the sodium and potassium salts of the acids from animal and vegetable fats), calcium resinate and oleate, aluminum oleate and palmitate, and the various soaps made from tung oil. The lead and manganese salts of organic acids, while technically soaps, are not considered under this heading because they are used more particularly for the purpose of accelerating the drying of the drying oils in the vehicle.

There is little scientific information available as to the effect of these various soaps on ink compounds. Certain desirable working qualities have been obtained and this is sufficient to justify their use, even though the reason for their action is not known. Among other things it has been suggested that soap acts as a binder between the vehicle and pigment. It would seem as if the entire subject offers a promising field for thorough investigation.

## PIGMENTS

LAMPBLACK.—Turning now to the pigments, the most important of all is lampblack. This is produced by the burning of oils and fats with an insufficient supply of air for complete combustion. The soot formed is allowed to settle in large chambers, and is collected from time to time. For this burning, lamps are used the construction of which is so controlled as to burn no more carbon than is necessary to keep up the combustion. The temperature of the flame must be kept as low as possible to prevent its burning its own smoke, and more particularly to prevent the distillation of the oil from the lamp. The presence of any considerable quantity of oil in the black will give it a greasy, smeary appearance, and make it totally unfit for further treatment. Various devices have been invented to automatically control the oil supply, so as to avoid loss by evaporation and the consequent spoiling of the black. The use of hollow cylinders through which water is kept running has been found satisfactory. The flame from the lamps strikes the cold metal surface and deposits its soot, which is afterward brushed off and collected.

Lampblack prepared by either of the above processes, when properly carried out, will contain very little oil.

Still another method for the preparation of lampblack is to burn the oil in open pans and draw the soot into a series of chambers. By this method the finest particles, containing very little oil, will collect in the last chambers, while the chambers nearest to the burning oil will collect the heavier particles and most of the evaporated oil. In this way a number of grades of black are prepared in one operation.

It was formerly thought necessary to remove practically all the oil from the lampblack before incorporating the latter in an ink. This is now considered unnecessary and a needless expense. In the case of blacks intended for mixing with linseed varnishes it would probably be desirable to have as little oil as possible, but with those intended for use with mineral and rosin oils the removal of the oil from the black does not seem important enough to warrant the expense of the operation.

Lampblack may contain up to 10 per cent of volatile matter. When heated it gives off a gas or liquid which is usually acid, sometimes neutral, and in rare cases alkaline.

Gas Black.—A very different quality of black is prepared by the burning of gas with insufficient air for complete combustion. The soot is deposited on metal cylinders in very much the same way as lampblack from oil. The black produced by this process, known as gas black or carbon black, is practically pure carbon, containing only a trace of oil or volatile matter.

These two pigments, lampblack and gas black, would seem at first glance to be practically the same, and possibly for some purposes the differences between them are of no importance. This is not true when they are used in printing inks. Lampblack, when ground in a soft varnish, gives flow or length to an ink, whereas gas black tends to make the ink short. Lampblack has more opacity and less strength than gas black. There is a great difference in the undertones of the two. It is apparent, therefore, that they are so different in working qualities as to justify the statement that they are in reality two different pigments, each with its own distinctive qualities and uses.

Bone Black.—As its name would indicate, bone black is made from charred bones. These are ground until a fine powder is secured. It is evident that such a pigment can never reach the same degree of fineness as lampblack. Its use is confined largely to the plate inks, where its peculiar properties make it a very desirable pigment. Although in thick films it has a very deep black, it lacks strength. It is not a cheap pigment and so can not be considered an adulterant, but it is out of place in the ordinary, or surface, printing inks.

Magnetic Pigment.—Still another black pigment used in printing inks is artificial magnetic oxide of iron. This is made by a patented process, which consists essentially in precipitating ferrous salts with alkali, and after partially oxidizing the precipitate, washing and drying it. It has a good color and is quite permanent. There are no data available as to its covering power and strength.

If one were to print with merely a mixture of oil and black pigments, and sufficient ink were carried to mask the undertone of the pigment, the results would be similar, though not identical, for the various blacks. But such heavy inking is not the rule, so that in actual work the ink may be carried so lightly that the effect of the undertone is visible. Furthermore, what the public calls black is in reality a blue-black. Hence an ink maker must compensate for the color of his undertones in order to obtain a denser and purer black. This is accomplished by the use of various blue pigments, such as the iron blues, aniline dyes, or aniline pigments (lakes).

Iron Blues.—The iron blues are a mixture of the ferrocyanides and ferricyanides of iron and potassium. The discovery of these pigments dates back to the eighteenth century, when Prussian blue was accidentally discovered by Diesbach, a color manufacturer. It was some years before its true composition was established by chemical research.

When a ferrous or ferric salt is added to potassium ferrocyanide a pigment is precipitated, which, according to the materials used and their purity, will vary in color from a pale blue to a purple. The best known of these pigments is Prussian blue, obtained by adding a ferric salt to potassium ferrocyanide. In commercial practice the pure compound, ferrous ferricyanide—$Fe_7(CN)_{18}$—, is not obtained, but a mixture of a number of double cyanides. In addition, there seems to be more or less potassium ferrocyanide carried down with the pigment, and, owing to the fact that it is practically impossible to wash it out, it has been considered a part of the pigment.

Iron blues used in the manufacture of printing ink may be classified as follows:

*Bronze blue;* having a strong bronzy appearance, with a green undertone.

*Milori blue;* very slight bronzy appearance, with a strong green undertone.

*Chinese blue;* a deep blue, with a strong bronzy appearance and an undertone somewhat like the bronze blue, but inclining more to a red.

*Prussian blue;* practically no bronzy appearance, with a purple undertone.

These colors are classified more with regard to their color qualities than their chemical composition, the former being of much greater importance, particularly when it is considered that these blues may be used in preparing the chrome greens, when slight differences in color quality will have a marked effect on the green produced.

The iron blues have great tinctorial power and are quite permanent in printing inks. Air, sunlight, and acids do not affect them, but they are completely destroyed by alkalies. This fastness to light gives them great superiority over the aniline pigments, many of which fade very quickly in direct sunlight. It must be remembered, however, that there are a number of blue aniline pigments which are quite permanent to light. It is not uncommon to find both an iron blue and an aniline pigment in black printing ink. The amount of each present will depend largely upon the effect desired.

For the manufacture of colored inks two classes of pigments are used, the natural or artificial mineral pigments, such as vermilion, chrome yellow, ultramarine, etc., and the coal tar lakes and dyes.

Vermilion.—Vermilion is the sulphide of mercury, a brilliant scarlet pigment which seldom occurs in nature in sufficient quantities and pure enough to be used. Most of it is artificially prepared. It is extremely heavy and has good covering power, but a pound of ink made from this pigment will not give as many impressions as a pound of ink made from a lighter pigment of equal strength. This latter fact and its high cost make it too expensive for any but the very best inks. It is used where a brilliant and permanent red is desired.

It is now possible to secure red dyes or lakes which are as fast to light as vermilion, and this fact has materially cut down the use of the latter material. Vermilion is objectionable in that it will rapidly attack a copper electroplate, necessitating the use of nickel in place of the copper. It should never contain free sulphur, since the latter would seriously affect the color of a lead lake should the latter be used in the same ink.

Chrome Yellow.—Chrome yellow (lead chromate) is an artificial product prepared by the reaction of a salt of lead (usually the acetate) and sodium or potassium bichromate, or a mixture of the two. It is made in a number of shades varying from a pale canary-yellow through orange to a scarlet. The paler colors always contain more or less lead sulphate, which is precipitated with the pigment and is considered an essential part of it. The orange and scarlet pigments contain varying amounts of basic lead chromate, the deeper shades having the greater amounts of basic chromate.

Chrome yellow pigments are brilliant in tone, dense, with great strength and coloring power, and are considered quite permanent.

Chrome Green.—The term "chrome green" is extremely vague. Originally it meant the green oxide of chromium, but the latter is not in very extended use to-day in printing inks and the name is now generally understood to mean a mixture of chrome yellow with a blue pigment. The latter may be a milori blue, bronze blue, Prussian blue, or Chinese blue, all of them being iron cyanide pigments, all being made in essentially the same way from identical raw materials, but differing somewhat in shade of color. According to which one of these blues is used, the chrome green may be called milori green, bronze green, Brunswick green, etc. The term Brunswick green has also been applied to the oxychloride of copper, but its use in this connection is obsolete. Lead sulphate is present as a constituent of the chrome yellow and aluminium hydrate and precipitated barium sulphate may also be present. Prussian blue is frequently used to produce olive green. The darker shades of green may be made by the addition of varying amounts of black. Chrome green is an excellent color, although not very brilliant in tone. It is quite permanent to light.

Ultramarine.—The true ultramarine is the mineral lapis lazuli. This is too rare for practical use. What is commonly known as ultramarine is the artificially prepared pigment, made by heating together china clay, soda, sulphur, and charcoal. The constituents are intimately mixed, finely ground, and heated in an oven. The burning must be carefully controlled. The resultant blue mass is ground, washed free from alkali, and then put through a process of purification in order to get a uniform and satisfactory product.

Ultramarine is apt to be crystalline in nature, and works with difficulty. On account of the sulphur present it can not be used on copper electroplates, and the latter, as in the case of vermilion inks, must be replaced by nickel.

Coal-Tar Colors.—The coal-tar colors used are too numerous and their manufacture is too detailed an operation to warrant consideration at any length. They cover almost every conceivable shade of color. Many of them are, unfortunately, very fugitive, being easily destroyed by direct sunlight, and such pigments are of value only in work where permanence is not a matter of much importance. There are, however, some coal-tar pigments which are more permanent to light than many inorganic pigments, sufficiently so for any requirements in printing inks.

When an aniline dye is precipitated upon a metallic base, a pigment is obtained which is frequently more stable to light than the original dyestuff.

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These so-called lakes have wide application; for details as to their manufacture, consult the references given at the end of this circular.

Red Lakes.—The red lakes are of such great importance, particularly in the three-color and four-color processes, that without attempting to go into any great detail it seems desirable to present a few facts regarding them.

They are mostly of coal-tar origin and may be roughly divided into three classes, as follows: Derivatives of aniline; derivatives of naphthalene; derivatives of anthracene.

The aniline lakes are characterized by their brilliancy of color. They are strong tinctorially, but very fugitive.

The naphthalene lakes are not as bright in color nor as strong tinctorially as the aniline lakes, but they are much more permanent. This class includes the Para colors and the so-called "scarlets."

The anthracene lakes are rather dull in tone and weak tinctorially, but are extremely permanent. The madder and alizarine lakes belong to this class.

There are probably some other organic reds used in printing which are not included in these three classes, but the latter form the largest and most important part.

The choice of lake therefore becomes a matter of what is expected of the finished article. If permanency is of no importance, the aniline lakes would be used on account of their brightness of color, but for record purposes this brilliancy must be sacrificed and the more permanent scarlets, Para reds, madder, and alizarine lakes used.

## DRIERS

There is probably nothing in the manufacture of printing inks which is less understood than the question of driers. Authorities differ on almost every point, and the practical result is that every manufacturer follows his own ideas and the results of his own experience.

We have seen that linseed oil is a drying oil, but in the raw state the drying is a matter of days. Obviously this would not do for printing ink, where we desire a product dry enough to handle in a few hours at the most. Certain metallic bases and salts, principally those of lead and manganese, have the property of accelerating this drying. This property has also been claimed for a variety of materials,[4] but with the exception of the lead,

[4] See L. E. Andes, "Drying oils, boiled oils," etc., p. 136, for a complete list.

manganese, and possibly cobalt [5] compounds they are practically all useless when not absolutely objectionable.

No definite figures can be given as to the correct amount of drier to use; this must be worked out for each particular case. Some pigments possess considerable drying properties, while others retard drying, and allowance must be made for the amounts of such pigments present in the ink. This is particularly true of the iron blues, which accelerate the drying. In addition, the questions of temperature, atmospheric conditions, quality of paper, speed of press, etc., must each receive due consideration in determining the quantity of drier to be used.

The question of driers is one of real importance. The oil must dry rapidly, and yet not so rapidly that it will dry on the press. Under the circumstances undoubtedly it is best to define what the ink must do and leave it to the art and experience of the manufacturer to attain the result by any method he can.

### INK FORMULAS

It is impracticable to give precise formulas for printing inks; practice varies too greatly. The following will, however, give some slight idea as to the approximate composition of the more common types:

Web-Press Inks.—For newspaper work the vehicle is usually mineral oil, rosin oil, rosin, and soap, and the pigment is a cheap lampblack with possibly a very small amount of blue dye. For the better grades of web-press inks a thin linseed varnish may replace part of the rosin oil. The pigment will be about 20 per cent of the ink.

Flat-Bed Inks.—The flat-bed inks are about the same as the better grades of web-press ink, the oil being one-half to two-thirds rosin oil and rosin, the remainder linseed, the latter being a thicker oil than the one used in web-press inks. The pigment will be about 20 to 25 per cent and will consist of a fair grade of lampblack, with Prussian blue or aniline pigments or dyes, and frequently both.

Job Inks.—The job inks include many of the colored inks, where, of course, the proportions of vehicle and pigment vary greatly on account of the large differences in specific gravity of the different pigments. If we could express our percentages by volume instead of by weight, these differences would largely disappear. The vehicle should be largely, if not entirely, linseed varnish and hard gums. The pigment, if lampblack, will form

[5] Recently cobalt salts, such as the resinate, acetate, and linoleate, have been recommended, and those who have used them report a fair amount of success.

about 25 per cent of the ink; for colored inks it may go as high as 60 per cent.

Halftone Inks.—Halftone inks are generally used on hard, smooth-surfaced papers. At no time will the penetration of the paper by the ink be very great, and in some cases there will be scarcely any penetration. The vehicle in these inks must be carefully adjusted to the grade of paper. There must always be enough drying oil present so that the ink, although not carried into the paper, will in a very short time set sufficiently to permit of handling the printed sheets without risk of injury. The higher the class of work the finer the pigment must be to do satisfactory work. Owing to mechanical difficulties a coarse pigment can not be used to produce the finest results. Gas black possesses special advantages over other pigments for this class of work.

Halftone inks require a large amount of pigment, running frequently as high as 30 per cent.

Of course it must be understood that these figures are for inks of good quality. *It should be an axiom with a printer that poor quality is a poor investment at any time.* We have only to pick up a book in which each page has offset on the opposite page, or has some other fault equally objectionable, to realize that the amount saved in poor quality is incommensurate with the loss in value of the finished article.

## INK MANUFACTURE

The first step is the preparation of the vehicle. The oil is boiled or burned by one of the methods described later in the chapter on linseed oil. The rosin, or hard gum, whichever it is proposed to use, is broken into very small pieces and melted over a fire. When the mixture is homogeneous it is added gradually to the hot oil and the whole stirred thoroughly. This is then filtered through a cloth and allowed to stand in order that the smaller particles of dirt, which may have gone through the cloth, may settle. After a few days the clear varnish is drawn from the sediment.

This is, of course, only one of the many methods in use. Sometimes the rosin, in small lumps, is added directly to the oil, which is then stirred until solution is complete, or the oil may be slowly added to the melted gum.

The varnish is now ready for the addition of the pigments. These are first mixed in a mixer, or kneading machine, this part of the process being merely a stirring of the vehicle and pigments together. It does not bring the particles of pigment into as intimate a mixture as is desired. To attain this end the ink, after being in the mixing mill, is ground between rolls, the grinding being repeated until the pigment is thoroughly incorporated with the oil and the grit is entirely eliminated. The cheap inks are ground only once or twice, while the better inks may be ground half a dozen times or more. It is almost impossible to exaggerate the importance of this part of the process; it is the real ink making. Up to a certain point the more thorough the grinding the finer will be the texture and color of the ink. Too much grinding may oxidize the oil, giving it a "heavier body," and thus change the consistency of the ink.

The grinding mill consists of three horizontal rolls, which revolve at different speeds, the rear roll slowest, the front roll fastest. The ink from the mixing mill is fed between the rear and middle rolls, and is carried around by the middle to the front roll, where it is scraped off automatically. The differential speed gives the grinding effect and reduces the pigment to the finest division possible.

The rolls used in grinding are of several kinds. Granite rolls are preferred by many; others favor the smooth steel rolls. The grinding develops considerable heat, so that the varnish thins out to some extent. In order to test it properly it is necessary to spread a little on a cold slab, where it will set in a few minutes. Its consistency can then be determined with reasonable accuracy. To overcome this heating, steel rolls, cooled with running water, are used. Advantages and disadvantages are claimed for this method. In its favor it is said that the oil will oxidize less; there is less chance of damaging colored pigments; and the consistency of the ink will be practically the same as it will be when used on the press. On the other hand it is claimed that with a thinner varnish it is possible to grind the ink finer and in less time.

## RELATION OF INK TO THE PAPER

Any discussion of printing ink would be incomplete without some reference to paper. The results obtained depend so much upon the correct adjustment of these two factors that knowledge of one alone will not be sufficient.

For the rapid newspaper or rotary press the paper is fed into the machine in a continuous web. The paper used is a machine-finished printing paper, which receives no further treatment than the slight glazing which it gets on the paper-making machine. It is usually made of wood pulp, with a small amount of rosin sizing, and seldom contains any large amount of added mineral filler. Such a paper has a rough surface and possesses a high degree of absorption. The paper absorbs the ink in very much the same manner as if it were blotting paper; therefore it is not necessary to have any drying oil in the ink.

There is, of course, considerable difference between various makes of this grade of paper. If the fiber has been beaten very fine, or if any amount of filling materials is added, a fairly smooth paper will result, whereas a coarse fiber will give a rough surface. There will be a marked difference between the behavior of these two papers toward the same ink; the rougher one will need more ink on the type to get the same density of color. There will also be a marked difference in the absorption of ink.

One of the first differences noticed between web-press and flat-bed work is the speed at which the presses are run. The latter may occasionally run as high as 2000 to 3000 revolutions an hour, but the usual rate is very much below that. The paper used is either machine-finished printing, or sized and supercalendered.

For book work, if plain text is desired, a machine-finished paper will be used. In composition this paper will vary from all-wood pulp to what is termed "rag machine-finished paper," which may contain as much as 50 per cent rag stock. It is quite the exception to use an all-rag stock for this work.

In books or pamphlets, where illustrations are to accompany the text, the latter is printed on machine-finished paper, and the former on either coated or sized and supercalendered paper. The latter paper has approximately the same composition as the machine-finished, but will contain, in addition to a somewhat larger amount of rosin sizing, about 10 per cent of china clay or some such mineral filler. The smooth surface of this paper is obtained by passing it between heavy rolls, when, under the combined influence of heat and pressure, a glazed surface is obtained. On such paper the ordinary web-press or flat-bed inks will not work satisfactorily, and as a rule a halftone ink, the consistency of which is suitable for this work, is used. The illustrations are inserted during the binding.

The usual method for book printing is to use the machine-finished printing paper with flat-bed ink on the flat-bed press for small editions, and the rotary press with web-press ink for large editions. Where illustrations and text are desired on the same page, a flat-bed press, with sized and supercalendered paper and a halftone ink, is preferred, but this is not absolutely necessary, since good results can be obtained on the rotary press.

Job ink is generally used in printing on paper which is also intended for writing purposes. Such papers are usually made from rag stock, to which has been added, in addition to a certain amount of rosin, a further sizing of glue. Mineral fillers may be present, although as a rule they are not used. In this class of work there is very little absorption of the ink by the paper, and most of the drying effect must come from the ink itself; hence the vehicle should consist largely, if not entirely, of drying oil.

For halftone (or illustration) work, a coated paper is used. The paper itself is of comparatively little consequence, and is usually of wood pulp with considerable mineral filler. This is covered with a mixture of china clay and casein and, when dry, is glazed, the resulting surface being absolutely smooth. Such a surface is necessary in order that it may receive the impression from even the finest lines of the halftone plates. The ink remains on the surface entirely, and the varnish used must dry within 16 to 24 hours—i. e., overnight—so as to permit of safe handling the following day.

## OPACITY OF INKS

The question of the opacity of inks is always one of importance. According to the use to which the ink is to be put, it may be dense and opaque, or it may be translucent.

For ordinary printing on white paper it is desirable to have the ink as opaque as possible, since the ink does not need to be carried as heavily on the type to get a satisfactory impression. If, however, one is printing with a colored ink on colored paper, then opacity is of the greatest importance, since the color of the ink will be materially changed if the color of the paper shows through it.

With the three-color and four-color processes the reverse is true. The three-color process consists of printing in red, yellow, and blue, obtaining the intermediate or secondary colors by printing one color on another. The four-color process adds black to the three colors above mentioned. The first color printed may be opaque without affecting the results seriously, but the other impressions must be as translucent as possible.

With these facts in mind, it will be seen that an ink which is suitable for multicolor processes is not suitable for printing one color on a colored paper. The reverse is equally true, except as above noted, when the opaque ink is used for the first impression.

## NECESSITY FOR PROPER GRADES OF PAPER

It will be seen that each grade of ink is prepared to give satisfaction with a particular grade of paper. To secure the best results with any ink it should be used on the paper for which it is intended, and, furthermore, the paper itself must be of good quality. This, of course, refers only to cases where it is desired that the work to be turned out shall be of good quality, have a good appearance, and be more or less permanent; there is always a certain amount of work where almost anything will do, if it does not cost too much. If it is admitted that a poor ink will not work satisfactorily on any grade of paper, it must also be seen that a poor grade of paper will not work satisfactorily with any ink. A short ink (one having slight cohesion) will not give good results, no matter what sort of press or paper is used, unless the pressman stands by and keeps constantly pushing it up against the feed roll. Similarly, a paper with loose fibers would be constantly filling up the type, and in such cases the trouble would not be with the ink being too tacky but in the paper. It is evident that one factor depends on the other, and neither can be neglected with impunity.

It is not within the scope of this circular to deal with the testing of paper, but simply to point out the necessity of being sure that the quality of the paper is all that it should be and suited to the work on hand. This is so obvious that a single illustration will be sufficient to show its importance.

During the printing of some halftone illustrations at the Government Printing Office it was noticed that some of the sheets had a streaked appearance, which rendered them unfit for use. The trouble was at first supposed to be due to an inferior ink, but examination proved that the latter was satisfactory and all that could be expected. The examination of the paper was not so satisfactory. Small pit holes, visible only under the microscope, could be seen wherever there was a streak. They were probably caused by minute bubbles of gas in the coating mixture, and their occurrence in streaks was probably due to the action of the brushes in the coating machine. Whatever the cause, it was a problem for the paper manufacturer to solve. Difficulties with paper such as this might occur at any time and would probably not be noticed in the ordinary testing of the paper.

The point to remember in this connection is that trouble, when it does occur, is not always due to faulty ink. The paper is frequently at fault and will bear investigation. This is assuming that there are only two causes for trouble, ink and paper. It might be well to remember that presses, and even pressmen, are not always blameless.

## WHAT CONSTITUTES A GOOD INK

The question is frequently asked: What constitutes a good ink? To answer it correctly, one should know exactly for what purpose the ink is intended. This problem has received considerable attention at the Government Printing Office, and a set of requirements and tests for the various inks used there has been formulated. These are so comprehensive as to be worth printing in full.

### INK REQUIREMENTS OF THE GOVERNMENT PRINTING OFFICE

#### Requirements for a Satisfactory Test

##### WEB-PRESS INK

1. Nonseparation of Oil from Pigment.—The oil or varnish should not separate from the pigment either on the face of the type or in the fountain.

2. Transfer.—Ink should transfer from type to paper so as to leave face of type clean.

3. Tack.—Ink should have sufficient "tack" to dry rapidly, but should not pull the nap or face from the paper, nor the face from the roller.

4. Drying.—Ink should not dry on form, rollers, or distribution so that it may not be easily removable therefrom after standing overnight.

5. Spreading of Oil or Varnish.—The oil or varnish should not spread in the paper after printing.

6. Color.—The ink must dry a bright, solid *black*, not gray; it should not blister the face of the paper, and should dry rapidly enough to permit quick handling of printed product.

7. Quantity Required.—The weight of the amount used must be noted and averaged on a basis of 10000 printed pages.

##### JOB BLACK INK

1. Nonseparation of Oil from Pigment.—The oil or varnish should not separate from the pigment either on the face of the type or plates or in the fountain, but should be short enough to break up readily in the distribution and not "string."

2. Transfer.—Ink should transfer from type or plates to paper so as to leave the face of type or plates reasonably clean.

3. Tack.—Ink should dry hard on writing or bond paper to admit of easy handling at the press without damage or injury to the work, and should not pull the coating or face from the paper, nor the face from the roller.

4. Drying.—Ink should not dry on form, rollers, or distribution so that it may not be easily removed therefrom.

5. Offset or Smutting.—Must be able to carry sufficient color, print clean and sharp, without offset or smut on sheets falling on top from the press fly, or in piling the work; nor should the offset pile up on the draw sheet in backing up.

6. Color.—The ink must dry a deep, solid carbon (not aniline) black, and not turn gray nor have a metallic sheen or luster, nor blister the face of the paper.

7. Quantity Required.—The weight of the amount used must be noted and averaged on a basis of 5000 printed pages.

#### FLAT-BED BLACK INK

1. Nonseparation of Oil from Pigment.—The oil or varnish should not separate from the pigment either on the face of the type or cuts or in the fountain, but should be short enough to break up readily in the distribution and not "string."

2. Transfer.—Ink should transfer from type or cuts to paper so as to leave the face of type or cuts reasonably clean.

3. Tack.—Ink should dry hard on the machine-finished paper immediately to admit of easy handling without damage or injury to the work, and should not pull the coating or face from the paper, nor the face from the roller, nor blister the face of the paper.

4. Drying. Ink should not dry on form, rollers, or distribution so that it may not be easily removed therefrom.

5. Offset or Smutting.—Must be able to carry sufficient color, print clean and sharp, without offset or smut on the tympan when printing the second or reverse side of the sheet.

6. Color.—The ink must dry a deep, solid carbon (not aniline) black, and not turn gray.

7. Quantity Required.—The weight of the amount used must be noted and averaged on a basis of 5000 printed pages

#### HALFTONE BLACK INK

1. Nonseparation of Oil from Pigment.—The oil or varnish should not separate from the pigment either on the face of the type or cuts or in the fountain, but should be short enough to break up readily in the distribution and not "string."

2. Transfer.—Ink should transfer from type or cuts to paper so as to leave the face of type or cuts reasonably clean.

3. Tack.—Ink should dry hard on the paper in eight hours to admit of easy handling without damage or injury to the work, and should not pull the coating or face from the paper, nor the face from the roller.

4. Drying.—Ink should not dry on form, rollers, or distribution so that it may not be easily removed therefrom.

5. Offset or Smutting.—Must be able to carry sufficient color, print clean and sharp, without offset or smut on sheets falling on top from the press fly, or in piling the work.

6. Color.—The ink must dry a deep, solid carbon (not aniline) black, and not turn gray nor have a metallic sheen or luster, nor blister the face of the paper.

7. Quantity Required.—The weight of the amount used must be noted and averaged on a basis of 5000 printed pages.

### Methods to be Used in Making Practical Tests

#### WEB-PRESS INK

The practical test of web-press ink shall be made on the web presses in use in the Government Printing Office.

The test shall be made on machine-finished book paper of the size, weight, and quality in general use in the Government Printing Office.

The type forms or plate forms shall be previously "made ready" and the press otherwise in good condition to make a satisfactory run.

The form, rollers, distribution, and ink fountain shall then be thoroughly washed and cleaned. The ink to be tested shall be weighed before being placed in the fountain. The quantity to be tested should be sufficient to run not less than three hours, and preferably a five-hour run will be made.

The press, form, rollers, and distribution will be permitted to stand overnight unwashed, in order to observe the drying on the face of the form, the rollers, and the distribution.

Ink that will separate the oil or varnish from the pigment on face of type or in the fountain will not be accepted.

Ink to be satisfactory should, under the impression, transfer from the face of the type to the paper, leaving the face of the type clean. It should have sufficient "tack" to dry rapidly, but must not pull the nap or face from the paper and leave it on the face of the type, or pull the face from the rollers. It should be easily removed from the type, rollers, and distribution after standing overnight. It should not contain oil or varnish which will spread in the paper after printing.

The ink to be satisfactory must dry a bright, solid black, and not turn gray or blister the face of the paper.

After the test has been made, the remaining quantity of ink shall be removed from the fountain and weighed, a reasonable allowance being made for the ink necessarily left in the fountain, on the rollers and distribution, in order to determine the number of copies a given quantity of the ink will print.

### JOB BLACK INK

The practical test of job black ink shall be made on the flat-bed presses in the Government Printing Office.

The test shall be made on book, writing, and bond paper of the size, weight, and quality in general use in the Government Printing Office.

The type or plate forms shall be previously "made ready" and the press otherwise in good condition to make a satisfactory run.

The form, rollers, distribution, and ink fountain shall then be thoroughly washed and cleaned. The ink to be tested shall be weighed before being placed in the fountain. The quantity to be tested should be sufficient to run not less than three hours, and preferably a run of five hours will be made.

Ink that will separate the oil or varnish from the pigment on face of form or in the fountain will not be accepted.

Ink to be satisfactory should, under the impression, transfer from the face of the type or plates to the paper, leaving the face of the type or plates reasonably clean. It should be heavy in body and feed well; it should have sufficient "tack" to dry rapidly enough on the paper while printing to avoid the necessity of using slip sheets, but it should dry hard on the paper quickly, so that the work can be easily handled without damage or injury to the printing. It must not pull the face or coating from the paper and leave it on the face of the form, or pull the face from the rollers. It should be easily removed from the form, rollers, and distribution; must be able to carry sufficient color without offset or smut, and print clean and sharp.

The ink to be satisfactory must dry a deep, solid carbon (not aniline) black, and not turn gray, nor have a metallic sheen or luster, nor blister the face of the paper.

After the test has been made, the remaining quantity of ink shall be removed from the fountain and weighed, a reasonable allowance being made for the ink necessarily left in the fountain, on the rollers and distribution, in order to determine the number of copies a given quantity of ink will print.

### FLAT-BED BLACK INK

The practical test of flat-bed black ink shall be made on the flat-bed presses in the Government Printing Office.

The test shall be made on machine-finished book paper of the size, weight, and quality in general use in the Government Printing Office.

The type or cut forms shall be previously "made ready" and the press otherwise in good condition to make a satisfactory run.

The form, rollers, distribution, and ink fountain shall then be thoroughly washed and cleaned. The ink to be tested shall be weighed before being placed in the fountain. The quantity to be tested should be sufficient to run not less than three hours, and preferably a run of five hours will be made.

Ink that will separate the oil or varnish from the pigment on face of form or in the fountain will not be accepted.

Ink to be satisfactory should, under the impression, transfer from the face of the type to the paper, leaving the face of the type reasonably clean. It should be heavy in body and feed well; it should have sufficient "tack" to dry rapidly, so that the work can be easily handled immediately without damage or injury to the printing. It must not pull the face from the paper and leave it on the face of the form, or pull the face from the rollers. It should be easily removed from the form, rollers, and distribution; must be able to carry sufficient color without offset or smut on the tympan when printing the second or reverse side of the sheets, and print clean and sharp.

The ink to be satisfactory must dry a deep, solid carbon (not aniline) black, and not turn gray, nor blister the face of the paper.

After the test has been made, the remaining quantity of ink shall be removed from the fountain and weighed, a reasonable allowance being made for the ink necessarily left in the fountain, on the rollers and distribution, in order to determine the number of copies a given quantity of ink will print.

### HALFTONE BLACK INK

The practical test of halftone black ink shall be made on the flat-bed presses in use in the Government Printing Office.

The test shall be made on coated book paper of the size, weight, and quality in general use in the Government Printing Office.

The type or cut forms shall be previously "made ready" and the press otherwise in good condition to make a satisfactory run.

The form, rollers, distribution, and ink fountain shall then be thoroughly washed and cleaned. The ink to be tested shall be weighed before being placed in the fountain. The quantity to be tested should be sufficient to run not less than three hours, and preferably a run of five hours will be made.

Ink that will separate the oil or varnish from the pigment on face of form or in the fountain will not be accepted.

Ink to be satisfactory should, under the impression, transfer from the face of the type or cuts to the paper, leaving the face of the type or cuts reasonably clean. It should be heavy in body, feed well, and have the consistency of new butter; it should have sufficient "tack" to dry rapidly enough on the paper while printing to avoid the necessity of using slip sheets, but it should dry hard on the paper in eight hours, so that the work can be easily handled without damage or injury to the printing. It must not pull the face or coating from the paper and leave it on the face of the form, or pull the face from the rollers. It should be easily removed from the form, rollers, and distribution; must be able to carry sufficient color without offset or smut, and print clean and sharp.

The ink to be satisfactory must dry a deep, solid carbon (not aniline) black, and not turn gray, nor have a metallic sheen or luster, nor blister the face of the paper.

After the test has been made, the remaining quantity of ink shall be removed from the fountain and weighed, a reasonable allowance being made for the ink necessarily left in the fountain, on the rollers and distribution, in order to determine the number of copies a given quantity of ink will print.

These requirements and tests are, of course, ideals, which are not always fulfilled in practice, yet it is the unanimous opinion of the pressmen of this plant that if they could secure inks which measured up to these standards there could be no cause for dissatisfaction.

There is some explanation which might be made of these tests. In rating an ink for "tack" it should be remembered that an ink can be poor by reason of too much or too little tackiness, and one defect is about as bad as the other. It should always be stated in which direction the trouble lies. The same is true of the drying; it should be specifically stated whether the ink is not drying rapidly enough, or if the fault is in the opposite direction, such as drying on the rolls, distribution, etc. A case is reported where a pressman stated repeatedly that the tack was poor, but gave no further explanation, and before the manufacturer was finally aware of the nature of the trouble he was producing an ink with the tackiness of glue.

The requirements for tack in test No. 3 state how rapidly the ink must "dry." Some printers and ink manufacturers use the term "set" in this connection, reserving the term "drying" for the final hardening of the ink. This explanation will probably suffice to prevent misunderstanding.

The ideal ink, one which will be satisfactory under any and all circumstances, does not exist, and probably never will. The mere fact that so many different inks are made should suffice to prove that the experience of the printers and ink makers has shown the necessity for suiting the ink to the paper. Since this is the case, it is obviously to the advantage of all for the printer to keep his ink maker informed as to the paper upon which the ink is to be used. This is particularly true of the small lots made up for special jobs. Cooperation along these lines would be of great advantage to everyone in eliminating trouble, saving time, labor, material, etc.

It might not be out of place to remark that no printer should ever try to improve upon his ink in order to remedy a fault. He should endeavor, in the first place, to buy an ink suited to his work. If the ink purchased is unsatisfactory the ink maker should be compelled to deliver the proper grade of ink, or point out that the ink ordered is not suited to the work in hand.

Tinkering with an ink, such as the adding of glycerin or vaseline to make it work better, should be resorted to only under exceptional circumstances, and whenever it is done the ink should be absolved from any trouble which may be caused by these "improvements." It is far better to have a variety of inks at hand, sufficient for any contingency that may arise, than to make one ink fulfill the purposes of many.

## ANALYSIS OF PRINTING INKS

This Bureau has already published an article on this subject, so that a brief summary of the methods described therein should suffice for those who have but a general interest in the chemical analysis of printing inks. Others are referred to the original article for full details.

Using as the solvent a mixture of benzene and ethyl ether, the oil is separated from the pigment by means of a centrifuge. In some cases petroleum ether may be used as the solvent. This method gives an effective separation, and the pigment may be determined with a fair degree of accuracy.

The oil fraction, after evaporating off the solvent, is analyzed for unsaponifiable oils (rosin and mineral oils), rosin, and linseed oil. No distinction is made between the unsaponifiable oils, rosin, and mineral oils.

In the black inks the pigment is ignited and the ash tested for lead and manganese oxides, which indicate the presence of driers, and for ferric oxides, the residue left on the ignition of iron blues. A qualitative test for iron blues is given, which will detect less than 1 per cent of this material in the pigment. If aniline dyes are present, they may be determined by extraction by means of alcohol, unless preliminary examination shows that the dye is insoluble in this solvent. In the latter event a suitable solvent must be found.

The colored inks require a preliminary examination to determine the nature of the pigment used, and the method of attack depends largely upon the results of these tests. Some of the mineral pigments, such as vermilion and chrome green (i. e., the material known commercially as milori or Brunswick green), may be determined quantitatively according to the procedure outlined in the original article. If the coloring matter consists of aniline dyes or lakes, it will usually be sufficient to determine whether or not these colors are fast to light. Two methods for this test are given.

A table is given showing how closely one may expect duplicate determinations on the same sample to check. These figures are the result of testing several hundred samples of ink by at least half a dozen analysts, so that they may reasonably be taken as a fair measure of the accuracy of the method. The accuracy obtained is all that could be expected of this class of material. To attain a higher degree of precision would demand more time and care than the results would warrant. There is certain to be more or less variation in two lots of ink prepared by the same maker, and yet such differences would have little or no effect on the working qualities of the ink. If, therefore, the results obtained by the chemist check at least as closely as the manufacturer can duplicate his product, they should be considered satisfactory.

## RELATION OF LABORATORY TESTS TO TESTS UNDER WORKING CONDITIONS

The practical tests and laboratory analyses have both been considered, and the question now arises, How much reliance can be placed on each? Ordinarily, the practical tests would be considered of greater importance, for it must be realized that if an article does all that is required of it, its composition is of minor importance. The laboratory tests should be used to supplement the practical tests, with the idea of learning whether the ink contains anything injurious to itself or to the paper, although it may seem to work satisfactorily. Used in this fashion, their aid to the scientific printer should be invaluable.

As an example, consider one of the old methods for testing the quality of halftone inks. A printed sheet is covered with alcohol and the quality judged by the blue color. Prussian blue is insoluble in alcohol, therefore all that this test really shows is the presence of certain blue dyes, which, if fugitive to light, would add nothing to the life of the ink. The oil may be pure linseed or it may contain rosin and rosin oil. Obviously, such a practical test has little value. Some of the dyes dissolve with a bright blue color, yet in dry form they may be green or bronzy in appearance. This bronzy finish may be desired, but laboratory tests alone will show whether the blue pigment used is permanent or not.

It is probable, however, that the greatest use of the laboratory tests will be in ascertaining the cause of trouble in printing. These methods have been used a number of times at this Bureau in just such work, and the success obtained leads one to believe that their wider application would mean greater usefulness along this line.

## MANUFACTURE AND TESTING OF LINSEED OIL

The United States is not only the largest manufacturer and consumer of linseed oil, but is second in the production of flaxseed, being surpassed in this latter respect only by the Argentine Republic.

The first step in the manufacture of linseed oil is grinding the seed. The latter is fed into the top of a stand of rolls, usually five in number, the pressure used being simply that of the weight of the rolls, and as the seed descends it is subjected to a constantly increasing pressure which crushes it into a fine meal. The ground seed is then tempered; that is, heated for some time in a closed kettle, steam being admitted from time to time to maintain the necessary amount of moisture in the seed. If the seed is very old and dry, it may even be necessary to add water.

The tempered meal is then formed into cakes, and these are placed in a press and subjected to hydraulic pressure of approximately 600 pounds to the square inch. After this pressure has extracted about all the oil that it can, the pressure is increased to about 3800 pounds. The total time for pressing is usually somewhat less than an hour. The pressed oil is run off in wooden troughs to the receiving tanks.

Linseed oil, as it comes from the press, contains a large amount of sediment, or "foots," which must be entirely removed if the oil is to be used for making printing-ink varnishes. For painting, the complete removal of foots is not so important, although the quantity should be reduced to the lowest practicable limit. Filter pressing the oil after it has cooled will remove a considerable amount of foots, and then storing the oil for some time in settling tanks will remove most of the remainder and give a comparatively clear oil.

If it is not desired to wait for this settling process, rapid methods may be used to refine the oil. Sulphuric acid is one of the most commonly used agents, the differences between the various methods being principally in the manner of removing the acid after the refining and bleaching are accomplished. The complete removal of the mineral acid is obligatory. When a light-colored varnish is desired, the raw oil must be practically neutral. Neutralizing the organic acidity of the oil with alkali, and then filter pressing, will give a clear neutral oil. These rapid processes for refining linseed oil all have a more or less injurious effect on its quality, and experience has shown that a well-settled oil is to be preferred.

Several new processes for extracting linseed oil from the seed have been developed, consisting essentially in removing the oil from the seed by means of certain solvents, such as naphtha, carbon bisulphide, etc., the solvent being distilled off from the oil, condensed, and used for further extraction. The loss of solvent by this method is very slight, and the resultant oil is of very good quality and comparatively free from foots. Some oils are practically ready for immediate use for varnish making. The fire risk seems to be one of the greatest hindrances to the extension of this process. The use of noncombustible solvents, such as carbon tetrachloride, is being tried, with some measure of success.

Linseed oil has the property of combining with the oxygen of the air, on exposure in thin layers, the final result being the formation of a hard film. The oil is changed into linoxyn, and the process is termed "drying." The rate of the drying may be increased by any of the following methods: Mechanical treatment of the oil, aging of the oil, raising of the temperature, exposure to sunlight, and addition of certain driers.

From a technical point of view the most important of these methods is the use of driers, the product being known as boiled oil. The oil is heated and stirred to thoroughly remove the moisture; the drier (containing usually compounds of lead and manganese) is introduced and the two are thoroughly mixed. The oil is kept at a high temperature for some time after the addition of the drier, although the longer the oil is heated the darker it becomes. When the process is deemed complete the oil is cooled and filtered through filter presses, the result being a dark, mobile oil which will, when exposed to the air in thin films, dry in about 24 hours. This oil is not used to any great extent in ink manufacture.

Raw linseed oil, or boiled oil, when placed on a clean sheet of paper will instantly sink into the paper, leaving a greasy stain. The oil must therefore be so changed that such penetration will not take place. There are two processes for accomplishing this, boiling and burning. The raw material is neutral raw linseed oil, free from metallic driers.

The boiling process for making linseed varnish consists in heating the oil in a tall cylindrical kettle, which is sometimes provided with a wide flange or basin on the side to prevent the oil, should it froth over, from reaching the fire. A tight-fitting cover is also provided, and the whole so arranged as to be quickly and easily removable from the fire. In some cases the kettle is stationary and the fire removed from under the kettle. The oil must be heated until a sample withdrawn from the kettle shows, upon cooling, that it has reached the desired consistency.

The temperature must be carefully regulated. Each kettle is provided with a thermometer, and the variation in temperature is kept as low as possible. The usual temperature is about 575° F (302° C). The time varies greatly with different raw oils, so that no definite time of heating can be specified. About 10 grades of varnish are made by this process, from No. 0000, a very thin varnish, to No. 7, which has the viscosity of molasses. These varnishes are used in making the ordinary printing inks. The thinner oils are used in inks for fast work, such as web-press inks, while the thicker oils are used in the job and halftone inks, which are used on the slower presses. It is seldom that an ink is made from a single varnish; to get the desired working qualities it may be necessary to use two or more.

The loss in oil by this boiling process is very small. If a clear, neutral oil has been used, a light-colored product will be obtained. However, the color of the oil is of little importance if the ink made is black.

The other method for preparing linseed varnish—burning—is practically the process first used in making printing inks. Oil is heated in small open kettles and then ignited. It is allowed to burn, with constant stirring, until the desired consistency is reached. A strong draft must be provided to carry off the fumes and soot produced by the burning. The loss during the burning is considerable, being from 5 per cent up. There are not so many grades of varnish made by this process, five being the usual number.

Burnt oils are usually called plate oils, because they are used almost exclusively in the preparation of engraver's ink. In the engraving process the plate is inked and the excess of ink is wiped off. In order that the plate shall be clean it is necessary for the ink to have but slight cohesion, or be "short." Stringing, or length, is objectionable. Varnishes made by the burning method are much shorter than those prepared by boiling, hence their use in engraving ink.

There are a number of tests applied to animal and vegetable oils which give practically constant results on pure material. The various constants of raw linseed oil have been very carefully determined by a number of chemists, at the request of the American Society for Testing Materials,[6] and as a result of their tests, extending over a number of years, the following limits were adopted for raw linseed oil made from North American seed:

| | Maximum | Minimum |
|---|---|---|
| Specific gravity at 15.5° C | 0.936 | 0.932 |
| Specific gravity at 25.0° C | .931 | .927 |
| Acid number | 6.00 | ........... |
| Saponification number | 195 | 189 |
| Unsaponifiable matter | 1.50 | ........... |
| Refractive index at 25° C | 1.4805 | 1.4790 |
| Hanus iodine number | ........... | 178 |

[6] Report of Committee E, Subcommittee on Linseed Oil, A. S. T. M., 9, 1909; Proc. A. S. T. M., 11, 1911; Vol. 13, 1913.

The burning of the oil produces great changes in these constants. The following figures will give some idea of the extent of these changes:[7]

| | Sp. gr. at 15° C | Free acid | Saponification number | Unsaponifiable matter | Hübl iodine number |
|---|---|---|---|---|---|
| Raw oil | 0.9321 | 0.85 | 288 | .......... | 169.0 |
| Tint | .9584 | 1.46 | 284 | .......... | 113.2 |
| Thin | .9661 | 1.76 | 285 | 0.62 | 100.0 |
| Middle | .9721 | 1.71 | 284 | .85 | 91.6 |
| Strong | .9741 | 2.16 | 294 | .79 | 86.7 |
| Extra strong | .9780 | 2.51 | 297 | .91 | 83.5 |
| Burnt thin | .9675 | 6.93 | 287 | 1.35 | 92.4 |

It will be seen that the burning increases the specific gravity, acid number, and saponification number, and largely decreases the iodine number, the latter figure showing the greatest variation.

Kitt[8] reports the following figures:

| | Acid number | Saponification number | Hübl iodine number |
|---|---|---|---|
| 0 | 4.8 | 188.9 | 159.3 |
| 1 | 5.2 | 188.9 | 101.4 |
| 2 | 7.8 | 189.1 | 95.6 |
| 3 | 9.5 | 186.6 | 83.6 |
| 4 | 9.1 | 187.2 | 79.1 |
| 5 | 11.7 | 187.2 | 76.2 |
| 6 | 18.8 | 192.3 | 71.1 |

It will be seen that, while the figures given above do not agree very well with those of the preceding table, they show approximately the same change, both in direction and amount.

The iodine numbers which have been published for linseed varnishes have all been determined by the Hübl method. This method has been supplanted almost entirely in late years by the more rapid Hanus method.[9] While the two methods are very similar, the results obtained are not comparable except in a very general way. In attempting to arrive at a value for linseed varnishes by the Hanus method great difficulty was experienced in getting satisfactory results. This method has been very carefully standardized for raw oil, but there has been little or no work done on the linseed

[7] F. H. Leeds, J. S., Ch. I., 1894, p. 204.

[8] Chem. Rev. Fett u. Harz Ind., 1901, 8 (3), pp. 40–42; abstracted in J. Soc. Chem. Ind., 1901, p. 484.

[9] A complete description of the Hanus method will be found in Bull. 107, Bureau of Chemistry, U. S. Dept. Agr. (rev ed.), p. 136.

varnishes. Preliminary work showed that the same conditions which hold for raw oils do not obtain for linseed varnishes. An investigation [10] was made to ascertain just what effect the different variables have on this determination and if possible to so define the method that comparable results could be obtained. It was found that comparable results could be obtained only when a prescribed method was followed exactly as regards weight of oil, amount and strength of Hanus solution, time and temperature of absorption, etc.

## BIBLIOGRAPHY

It is manifestly impossible, in a circular of this kind, to give complete details of everything under discussion. There will be many, however, who desire to take up the question of printing inks further and at greater length, and for their benefit a list of books on inks, oils, and pigments is given below. Many of these books have been freely consulted in the preparation of this circular, so that due acknowledgment of the help derived from them is in order.


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