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ANALYSIS OF PRINTING INKS

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I. INTRODUCTION

Some years ago the Government Printing Office requested the Bureau of Standards to make an analysis of several of the printing inks which they were using. A search of the literature failed to reveal anything which would be of material assistance. The procedure which was devised for making these tests has been revised and amplified from time to time, and in the form in which it is given below has been in use for two or three years. The results of these tests have been so satisfactory that the procedure is now given in the hope that it may be of service to those who, without any previous experience, may be called upon to analyze printing inks.

II. COMPOSITION OF PRINTING INKS

In view of the fact that this bureau is now preparing a circular of information on the general subject of printing inks, it is not considered necessary to discuss here at length the composition of printing inks. In this circular it is proposed to give the composition of the more common types of ink, and those who are interested in this phase of the subject will doubtless find there the information they may need. Suffice it to say that the oil may contain linseed oil, mineral oil, rosin oil, hard gums, rosin, and soaps. The pigment of the black inks may contain ivory black, carbon black, lampblack, magnetic pigment (artificial magnetite), bone black, Prussian blue, aniline dyes and lakes, oil driers, and mineral fillers of various kinds. The pigments in the colored inks are usually the common mineral pigments and aniline lakes. A few qualitative tests will show which ones have been used.

III. PROCEDURE OF ANALYSIS

The purpose of the following scheme of analysis is to ascertain the approximate composition of the inks and to prove the presence or absence of injurious materials. It is therefore not at all necessary that the analysis shall be of the highest accuracy, and indeed it is just as well to admit now that with a mixture of as many materials as we have in printing inks such accuracy is entirely out of the question. Where two or more methods are available, preference is given either to that method which is the shortest, or which most easily permits of combination with methods for the determination of other constituents. The result has, on the whole, been very satisfactory, although there have been times when greater accuracy would perhaps have been desirable.

It is not necessary in every case to run through the entire scheme of analysis for any particular ink; frequently a few qualitative tests, combined with several practical tests on the press, will give all the information desired.

1. SEPARATION OF OIL AND PIGMENT

We shall first divide the components of printing inks into two classes, oils and pigments. Separation of these two is readily effected by means of the proper solvent, or a combination of solvents.

The first solvent tried was petroleum ether, which was found to be very satisfactory with certain grades of ink, particularly web-press and flat-bed inks, but with the better inks it gave a very poor separation. Ethyl ether and benzene were both tried and each had its good points, but the best results were obtained, all classes considered, by using a mixture of three parts of ether to one part of benzene. Separation by the method of settling was tried; adding the solvent to the ink in a tall cylinder, stirring thoroughly, and allowing the pigment to separate out after standing, decanting the clear solution and repeating with fresh portions of the solvent until all the oil was removed. This was found to be too long a process for satisfactory use. Centrifuging was then tried and found satisfactory. The method as finally adopted is as follows:

About 50 grams of ink (avoiding the hard film which frequently forms on the surface) is placed in a weighed glass tumbler of about 300-cc capacity, a small amount of solvent added, and the whole stirred thoroughly until a homogeneous mixture is obtained. The glass is then filled with the solvent to within about half an inch from the top, and the whole again stirred. It is next placed in the metal cup of the centrifuging machine, and the space between the glass and metal cups filled with water in order to equalize the pressure of the liquid inside the glass during the centrifuging. Placing a rubber disk at the bottom of the metal cup has been found to materially lessen the danger of breakage during the operation. The metal cup and contents are then exactly counterbalanced, most conveniently by either a second sample of the same ink or another sample of ink, and then both are placed in the machine. For web-press and flat-bed inks 2000 revolutions per minute for 10 minutes is sufficient for a complete separation. Where carbon black has been used it has frequently been necessary to run the machine at 2600 to 2800 revolutions per minute for 20 or 30 minutes before a satisfactory separation is secured. The clear liquid is decanted through a pleated filter into a glass bottle, a further quantity of solvent added, and the process repeated. Usually three treatments suffice to give practically complete separation of oil and pigment. The glass and contents are dried at about 90° C and on cooling

reweighed. The increase in weight is the pigment, which is calculated to percentage. The amount of pigment on the filter paper should be negligible if the centrifuging has been efficient.

This method will not always yield results of great accuracy. The errors, which vary in magnitude with different inks, are as follows:

Some of the dyes are soluble to some extent in the solvents, tending to give low results for pigment.

Hard gums may not be completely soluble, and thus part will remain with the pigment.

The hard scum (linoxyn) which forms on the surface of the ink after it has been exposed awhile, is difficultly soluble and remains with the pigment. This should be excluded in sampling, for if it is not done a considerable error may be introduced.

Carbon black contains some particles so fine that it is impossible to cause them to settle, even in the centrifuge.

The net error of this determination is therefore the algebraic sum of these various errors.

2. ANALYSES OF THE OIL

The oil fraction may contain linseed oil, hard gums, rosin, rosin oil, mineral oils, and bituminous substances. The last mentioned, when present, must be judged largely by their color; being a mixture of a number of different substances of varying chemical nature, the determination of the total amount present is a matter of too much difficulty to justify the time required.

Determining the various constants, such as iodine number, saponification number, acid number, etc., does not give very reliable data regarding composition. If there were but two components, the proportion of each might be determined at least approximately in this way, but with three, and sometimes more, substances present, such determinations are useless, even if the constants of the individual substances are well known. We are therefore forced to rely upon qualitative tests, supplemented by quantitative determinations of some of the more important constituents.

We have found it convenient to regard the oil fraction as consisting of hard gums, rosin, unsaponifiable matter, and linseed oil.

The hard gums are difficult to determine, the only method which has given any measure of satisfaction being that of McIlhenny.[1] This method depends upon the insolubility of hard gums in water and petroleum ether. The method is much better adapted for the analysis of paints than printing-ink varnishes, but it can be used for the latter to obtain some idea of the amount present.

The general procedure adopted in this Bureau, for the analysis of the oil fraction, is as follows:

Sufficient of the solution from the separation of the oil and pigment to leave a residue of about 5 grams is evaporated in a weighed beaker; 50 cc of normal alcoholic potash is added, the beaker covered with a watch glass, and heated on a steam bath for several hours, stirring frequently to assist saponification. When the latter is complete the watch glass is removed and the alcohol distilled off. The residue is transferred to a separatory funnel with successive portions of water, using in all about 100 cc, and extracted with petroleum ether until no further oil can be extracted. Four extractions are usually sufficient. The petroleum ether fractions are united in another funnel, washed with water until the wash water gives no further alkaline reaction, filtered into a weighed beaker, the petroleum ether distilled off, and the residue dried at 95° C, cooled, and weighed. If this unsaponifiable matter is over 2 per cent, it indicates the presence of something else than linseed oil and hard gums. The wash water from the first two washings should be united with the water layer in the first separatory funnel.

This unsaponifiable matter is tested for the presence of rosin oil. The most satisfactory method of testing qualitatively for this material is the Liebermann-Storch test, which consists in heating a small portion of the oil with 10 cc of acetic anhydride, allowing it to cool, and adding a drop of sulphuric acid, sp. gr. 1.63. A violet coloration indicates rosin oil. It is always best to run a check test at the same time with some pure rosin oil or rosin. The test is identical for the two materials.

If the test for rosin is positive, the alkaline water solution which has been extracted with petroleum ether is made acid with hydro-

[1] P. C. McIlhenny: Chem. Eng., 8, p. 70, 1908; Chem. Abs., 2, p. 2630, 1908.

chloric acid (there is usually sufficient dye present from the ink to act as indicator), and the fatty acids which are thus liberated are extracted with successive portions of ethyl ether. These extracts are united, washed free from acid and salts, and evaporated in a small beaker.

A quantitative determination of the rosin can be made by either the Twitchell method, which depends upon the separation of the esters of the fatty acids, or by Gladding's method,[2] which depends upon the separation of the silver salts of these acids.

A very satisfactory method, and the one which is used here, is the modification of the Gladding method suggested by E. J. Parry.[3] The fatty acids are dissolved in 20 cc of 95 per cent alcohol, a drop of phenolphthalein is added, and then strong caustic soda (one part alkali to two parts water) until the reaction is just alkaline. The solution is heated for a few minutes, allowed to cool, and then transferred to a 100-cc stoppered graduated cylinder. The latter is filled to the 100-cc mark with ether, 2 grams of powdered silver nitrate crystals is added, and the mixture shaken vigorously for 15 minutes, in order to convert the acids into their silver salts. When the insoluble salts have settled, 50 cc of the clear solution (containing the silver salts of rosin) is pipetted off into a second 100-cc cylinder, and shaken with 20 cc dilute hydrochloric acid (one acid to two water). The ethereal layer is drawn off, and the aqueous layer is shaken twice with ether. The ether extracts are united, washed with water, and the ether distilled off in a weighed beaker. The residue (rosin) is dried at 110° to 115° C, cooled, and weighed. The results are calculated on the basis of the original weight of the oil.

The difference between 100 per cent and the sum of the unsaponifiable matter (if over 2 per cent) and the rosin may be considered linseed oil.

3. ANALYSIS OF THE PIGMENT

(a) BLACK INKS

The first step in the analysis of the pigment of a black ink is to ignite a weighed quantity in a porcelain crucible (platinum can not be used on account of the lead which is usually present). The

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[2] Am. Chem. J., 3, p. 416. 1881–82.   [3] Allen's Commercial Organic Analysis, 4th ed., Vol. V, p. 73.

ignition should be performed at the lowest possible temperature required to obtain complete combustion. This precaution is general, and applies to all inks. The loss on ignition represents lamp-black, the carbon of boneblack (should there be any present), aniline dyes, and undissolved oils or gums. Prussian blue is decomposed by heat, part of it being volatilized, the iron remaining as iron oxide. The residue from the ignition contains any added mineral matter of the pigment, lead or manganese from the driers, iron oxide from the Prussian blue, or iron oxide added as such (the so-called magnetic pigment), calcium phosphate if boneblack is present, and alkali or calcium carbonates from the soaps present. All ignitions of pigment must be performed under a hood having a strong draft.

The ash is analyzed quantitatively for insoluble matter, lead, iron, manganese, and calcium.

One-quarter gram of the ash is heated to dull redness in a porcelain crucible for a few minutes, cooled in a desiccator, and weighed. This is transferred to a 250-cc beaker, using concentrated hydrochloric acid to dissolve any material that may stick to the crucible. About 25 cc of concentrated hydrochloric acid is added, the beaker covered with a watch glass, and after heating until as much as will go in solution is dissolved, the cover is removed and the solution evaporated to dryness. The residue is moistened with a few drops of strong hydrochloric acid, 50 to 75 cc of boiling water added and the solution is filtered, washing thoroughly with hot water. The filter paper and residue are ignited and weighed, and the product is called "insoluble matter."

Fifty cubic centimeters of 10 per cent sulphuric acid is added to the filtrate from the previous determination and evaporated down until the solution fumes strongly. This is cooled, diluted carefully with about 100 to 150 cc of water, and heated on the steam bath until any basic ferric sulphate which sometimes separates is redissolved. The precipitate containing the lead sulphate is now filtered off. A small amount of lead sulphate will, in all probability, stay in solution, but inasmuch as the ash is seldom more than a few per cent of the entire ink, and of this only a

small amount is lead, the amount thus lost is negligible. The precipitated lead sulphate is dissolved in ammonium citrate or acetate, filtered from any insoluble matter, the filtrate made strongly acid with sulphuric acid, and the precipitated lead sulphate filtered off on a Gooch crucible, ignited, and weighed. We have used for this purpose a platinum Gooch crucible with a platinum felt, and found it extremely satisfactory. The insoluble matter from the ammonium acetate solution should be examined for calcium and barium.

Another method for the determination of the lead is to nearly neutralize the acid present with sodium carbonate, saturate the solution with hydrogen sulphide, filter off the precipitated lead sulphide, dissolve it in fairly strong nitric acid, and determine the lead as sulphate by the addition of sulphuric acid as above. In this case solution in ammonium acetate is omitted. The former method is of advantage where qualitative tests show that there is very little manganese present, and it is desired to determine only the iron. The filtrate from the lead sulphate leaves the solution in perfect condition for this determination. The iron is reduced to the ferrous condition by passing the solution through a Jones reductor, and the ferrous sulphate titrated with a standard solution of potassium permanganate, which has been standardized with sodium oxalate.

Iron is separated from manganese and other metals which may be present by precipitation with ammonia, the precipitate being filtered off, dissolved in hydrochloric acid, reprecipitated with ammonia, and again filtered. It is now dissolved in hydrochloric acid, sulphuric acid added, and evaporated down until all the hydrochloric acid is removed; the solution is diluted and the iron determined as before, with the Jones reductor. This method for determining iron is rapid and accurate. Before the addition of the ammonia, if hydrogen sulphide has been used, the solution should be boiled until all the hydrogen sulphide is removed, and nitric acid added to oxidize the iron to the ferric condition. In general, throughout the entire analysis, the usual precautions recommended by the various textbooks should be observed.

Hydrogen sulphide is now passed into the ammoniacal solution from the iron precipitation. This is allowed to stand over-

night, and the precipitate, if there is any, is examined for manganese. Usually there is only a trace of manganese, insufficient to warrant a quantitative determination. Should there be much manganese the sulphide can be filtered off, and the quantitative determination made by conversion into the pyrophosphate.

If it is desired to determine the calcium, this can be done after the filtration from the ammonium sulphide. (If phosphates are present—as, for instance, if bone black is present—a basic acetate separation is required.) In either case the lead should be separated by hydrogen sulphide. The filtrate from the manganese sulphide is heated on the steam bath until the hydrogen sulphide is removed, ammonia and ammonium oxalate are added, and the precipitated calcium oxalate is determined either as calcium oxide or sulphate.

The percentage of ash will be of great assistance in determining the nature of the pigment. Black oxide of iron is only slightly changed on heating, being completely oxidized to ferric oxide. Bone black is composed largely of calcium phosphate, yielding the greater part of its weight as ash. The presence of any large amount of phosphoric acid will be sufficient evidence that bone black has been used.

Prussian blue should be tested for qualitatively in the dry pigment. For this purpose 1 gram of pigment is moistened with 2 or 3 cc of normal alcoholic potash, heated on the steam bath until the alcohol is removed, 5 cc of water added, and the insoluble matter filtered off. The filtrate is made acid with hydrochloric acid, and filtered again if necessary. When ferric chloride is added, a blue precipitate will be obtained if Prussian blue is present. Sometimes sufficient blue dye goes through the filtrate to obscure the reaction. In this case the solution is again made alkaline and filtered. After filtration it is made acid with hydrochloric acid as before, and then copper sulphate is added. The precipitate is filtered and washed thoroughly. In this case we will have reddish-brown copper ferrocyanide. It is advisable, in case of doubt, to add a small amount of Prussian blue to the pigment, and make a check test.

In the absence of black oxide of iron we may assume that all of the iron in the filtrate is due to the Prussian blue. The per-

centage of Fe_2O_3 in the ash, multiplied by the percentage of ash in the pigment, multiplied by the factor 1.53, will give, roughly, the amount of Prussian blue present. The factor 1.53 is obtained by the ratio $Fe_7(CN)_{18}$ to Fe_2O_3. This is purely theoretical but is sufficiently accurate for the purpose.

Practically all of the dyes which are used in black printing inks are soluble in alcohol, so that an approximate determination can be made by extracting the dye with this solvent. For this purpose we have used an extractor of the Wiley type, in which the material is extracted by the solvent at its boiling point.

When the presence of oxide of iron is suspected, 1 gram of pigment is wrapped in filter paper and the dye extracted with alcohol, as in the preceding paragraph. When all of the dye has been extracted, the paper and contents are dried and the nitrogen is determined in the residue by the Kjeldahl method. From the nitrogen thus determined the Prussian blue is calculated, using the factor 3.41. The Fe_2O_3 present in this amount of Prussian blue, is deducted from the total Fe_2O_3 found in the ash. The remainder will be the percentage of iron from the magnetic oxide. The formula of the latter is theoretically Fe_3O_4, and the proper calculation should be made. This method for the determination of Prussian blue depends upon the fact that the aniline dye is the only other material which may contain nitrogen. Instead of calculating the Prussian blue from the amount of iron present, we determine it from the nitrogen remaining after the removal of the aniline dye. In this way both Prussian blue and magnetic oxide of iron may be determined with reasonable accuracy.

(b) BLUE INKS

A weighed quantity of pigment is ignited as under black pigments. The ash is analyzed by the same procedure as before, determining only lead, manganese, and iron if the qualitative tests show that Prussian blue is present. The lead and manganese are reported as metallic driers, the iron is calculated to Prussian blue, and the remainder reported as mineral filler. The composition of the filler, as a rule, is of no consequence.

The presence of ultramarine will be shown by the blue color of the ash. We have, unfortunately, no method for its quantita-

tive determination. In this case the ash is reported after deducting the lead and manganese.

Soluble aniline dyes are determined by extraction with alcohol, as under black pigments.

(c) RED INKS

The most brilliant red mineral pigment is unquestionably vermilion (mercuric sulphide). Its price prohibits its use in any but the best grades of red ink. It is very readily detected qualitatively by taking a small quantity of pigment, covering it with 4 or 5 cc aqua regia, and heating gently. This is diluted with five volumes of water, filtered, and stannous chloride added to the filtrate; a grayish precipitate of mercury will be formed if vermilion is present. A very small amount can be readily detected by this test.

The quantitative determination of vermilion, however, is much more difficult. The estimation of mercuric sulphide under the most favorable circumstances is a problem requiring both skill and experience. One method is to dissolve the mercuric sulphide in aqua regia, and after nearly neutralizing the diluted solution to precipitate the mercuric sulphide with hydrogen sulphide, and weigh the precipitate on a Gooch crucible, observing all the precautions to eliminate sulphur which separates during the precipitation.

The following procedure has also been found of value: One gram of the pigment is treated with a slight excess of ammonium sulphide. Sodium hydroxide is then added, while stirring. The beaker is placed upon the steam bath, adding more alkali if necessary, until all the mercuric sulphide has passed into solution. An excess of alkali should be avoided. The solution is allowed to cool, filtered, and the residue washed thoroughly. To the filtrate, sufficient ammonium nitrate to reprecipitate the mercuric sulphide is added, and it is then boiled to expel ammonia. The precipitate is allowed to settle, which takes but a short time, and the supernatant liquid decanted through a weighed Gooch crucible. The residual mercuric sulphide is boiled with a little sodium sulphite solution to remove free sulphur, and is then transferred to the crucible where it is washed with hot water until it no

longer reacts with silver nitrate solution.   It is dried at 110° and weighed.

The pigment is ignited, and the ash analyzed for lead and manganese.   The rest of the ash is reported as mineral filler.

(d) GREEN INKS

The coloring matter may be chrome green, green lake, or dye. Some of the darker shades are obtained by the addition of lampblack.   The ash of the pigment is determined as usual.   Part of this ash is taken and tested qualitatively for chromium.   If present, the ash should be tested for the following substances: $PbCrO_4$, $PbSO_4$, PbO, $BaSO_4$, $CaSO_4$, Fe_2O_3, and Mn_3O_4.   For the determination of sulphur, 0.250 gram of the ash and 5 grams of a mixture of equal parts of potassium nitrate and sodium carbonate are fused in a porcelain crucible over a sulphur-free flame.   The cooled mass is extracted with hot water and filtered.   The filtrate is acidified with hydrochloric acid, heated to boiling, and 10 cc 10 per cent barium chloride added.   After standing overnight, the precipitated barium sulphate is filtered off, ignited, and weighed as usual.   The solution should be sufficiently acid to prevent any significant contamination of the barium sulphate with barium chromate.

For the determination of barium, the insoluble matter is dissolved in hydrochloric acid, the solution made nearly neutral with sodium carbonate, and hydrogen sulphide is passed into the solution until all the lead is precipitated.   The lead sulphide is filtered off, the filtrate heated to boiling, and 10 cc of 10 per cent sulphuric acid added.   The barium sulphate is treated as directed under the determination of sulphur.

A fresh portion of ash is mixed with sodium peroxide and fused in a nickel crucible.   The cooled melt is dissolved in hot water and filtered.   Carbon dioxide is passed into the filtrate, and the latter heated again on the steam bath in order to precipitate any lead which may be held up by the caustic alkali.   Any insoluble matter which may separate is filtered off.   The filtrate is made strongly acid with hydrochloric acid, potassium iodide added, and the liberated iodine titrated with a standard sodium thiosulphate solution.   From the amount of thiosulphate used the amount of CrO_3 present is calculated.

The two precipitates from the previous determination are combined and used for the determination of lead, iron, manganese, and calcium. They are dissolved off the filter paper with hydrochloric acid, the solution is nearly neutralized with sodium carbonate, and hydrogen sulphide passed into the solution. The precipitated lead sulphide is filtered off, dissolved in nitric acid, and determined as sulphate, as directed under black pigments.

The filtrate from the lead sulphide is heated until all the hydrogen sulphide is boiled off. If any sulphur separates, it is filtered off. Two or three cubic centimeters of nitric acid is added and the solution again heated. It is then made alkaline with ammonia and filtered. The precipitate is dissolved in hydrochloric acid and reprecipitated with ammonia, the precipitate again filtered off and the filtrate united with that from the first precipitation. This solution is reserved for the determination of manganese.

The second precipitate of iron is dissolved in hydrochloric acid, converted into the sulphate, and the iron determined as under black pigments by reduction with the Jones reductor and titration with potassium permanganate.

The united filtrates from the iron precipitation are saturated with hydrogen sulphide, allowed to stand over night, and then filtered. If there be a sufficient amount of manganese present, it can be determined quantitatively as pyrophosphate; otherwise qualitative identification will be sufficient.

The filtrate from the manganese sulphide can be used to test for calcium, as directed under black pigments, if this determination is desired. It is seldom of value.

It is difficult to give precise directions for calculating the results from the preceding determinations. To a large extent the analyst must use his experience in deciding the various questions as they come up. It is probably safe to assume that all of the chromium was present originally as lead chromate, and it should be so calculated. The iron oxide should be calculated to Prussian blue, provided there is a positive qualitative test. Any barium present should be calculated to sulphate; if there is any question as to its being originally present as carbonate, the ash of the pigment is treated with very dilute hydrochloric acid, the solution filtered, and the filtrate tested for barium. Barytes is difficultly soluble in

cold dilute hydrochloric acid. In the absence of barytes the sulphur present is calculated to lead sulphate. The excess of lead over that required for the lead chromate and sulphate may be considered as drier.

China clay may be present, either as an added part of the chrome green, or as the base of a green lake. In such cases the undetermined portion of the ash should be reported as mineral filler.

Green dyes are determined by extraction as usual. In the absence of chrome green the pigment is ashed, and the ash analyzed for lead and manganese only, the balance being reported as mineral fillers.

If lampblack has been used to produce a dark shade of green, it can be tested qualitatively by taking a small portion of the pigment, treating it with strong alkali, and filtering through a Gooch crucible, washing first with hot water, and finally with moderately strong hydrochloric acid. Lampblack will show a black residue, which will disappear on ignition. No quantitative determination has been developed for this material, and it is generally classed with the volatile constituents, which are then reported as aniline dye, lampblack, undissolved oil, etc.

(c) INKS OF OTHER COLORS

The above classes represent the inks most used for ordinary work. If it is desired to test other colors, the general procedure would be simply to make qualitative tests for the pigments. The metallic driers present can be determined in the ash if so desired. Reference to the various textbooks on this subject may be of assistance in suggesting what materials may be present.

IV. RELATION OF ANILINE DYES TO THE PAPER

The soluble aniline dyes used in printing inks are usually of only secondary importance. They are present merely to neutralize the yellow color of the oil, and thus produce a deep black. Exposure to direct sunlight for a few hours is usually sufficient to destroy their color, so that for permanence, in so far as light is concerned, we must depend upon the Prussian blue, and it is for this reason that emphasis has been laid upon the determination of the latter pigment wherever it is present.

In the addition of aniline dyes to printing inks, there are several points to consider. If the dye is soluble in the oil, the amount so dissolved will have its true color. Where undissolved dye is present, it is necessary to know whether the dry powder has the same color as the dye in solution. For example, some of the blue dyes are blue in the dry condition, but others have a bronze or even a greenish color. These latter tones are particularly objectionable in halftone work.

In general, we may say that it is imperative that we should know whether the dye added to the pigment will produce unsatisfactory results. Some years ago the Government Printing Office had an experience which illustrates this point. In printing illustrations from halftone plates it was noticed that some sheets had a decidedly brownish color, while other sheets, printed on the same press and with the same ink, were perfectly satisfactory. A thorough examination of both ink and paper revealed the fact that the brownish color was due to insufficient coating of the paper. Around each fine point in the printing a brownish ring was formed, owing to the absorption of the oil by the paper. The color was intensified by the fact that the ink contained a yellow dye, which was fast to cellulose. In thus taking away the oil from the pigment the latter was left on the surface of the paper in a loosely adhering condition, and was easily brushed off, revealing the paper which had been dyed yellow. In the case of the sheets showing the normal color the coating was sufficiently strong to resist the penetration of the oil, which therefore dried on the surface without any unsightly effect.

We have here a combination of faults. There should be no separation of oil from pigment, although it is apparent that with a proper grade of coated paper such separation will not occur. The dye used in the ink was equally objectionable; it should have have been blue, and not yellow, and the dye should not have been fast to cellulose.

This particular case has shown the necessity of knowing whether the dye has any effect on the paper. This test is made by dissolving some of the dye from the pigment with alcohol and placing in this solution pieces of cotton thread. The solution is heated on the steam bath for about five minutes, the dye poured off, and the cotton washed thoroughly with hot alcohol. If the dyes are

fast to cellulose, they can not be removed from the cotton by this washing process.

With colored inks the question of importance is frequently not so much what dye or lake has been used, and how much, but how permanent it is. Exposure to light is the easiest method for determining this. This test is performed by making some streaks on white paper with the ink in question. These should be about half an inch wide and about 10 inches long. The film of ink should be as thin as it is possible to make it, and should correspond as nearly as possible to the thickness of the film of ink used in printing. The sheet is allowed to remain in a dark place for 24 hours to dry thoroughly, and is then divided into three parts. The middle section is exposed to direct sunlight until the color changes, or until it is apparent that no change will take place, 50 to 75 hours being about the right length of time. The two outside sections are kept in the dark for the purpose of comparison. After the exposure is completed the strips are joined together in their original position, when it is possible to detect very slight changes in color. A number of inks can be tested on the same sheet if so desired.

Another method for determining the relative permanency of different samples of the same color has been suggested.[4]

Flat tints of each ink are printed as strongly as if they were to be part of a color job. These tints should be about 5 by 7 inches in size. They should then be cut out to this size. If a photometer scale is then made of five layers of fine tissue paper, each layer 1 inch narrower than the preceding, this will give five different thicknesses of tissue, each thickness presenting a band 1 inch wide and 7 inches long. Across these and about 1 inch apart should be glued three strips of opaque black paper 1 inch wide and 5 inches long, starting 1 inch from and parallel to one narrow edge of the tissue paper. The photometer thus made, and a printed sheet of the ink to be tested, are then put into a photographic printing frame, which has a plain glass in the front of it. The whole is then exposed to the sunlight with an ordinary photographic printing-out photometer until the total exposure has reached a certain value on the photometer scale (usually the last number). When the printed sheet is taken from the frame it will

[4] Private communication from H. R. Gaylord, and Mr. Averill, of the State Institute for the Study of Malignant Disease, at Buffalo, N. Y., through E. S. Moores, of the Government Printing Office.

be found to be divided into three unfaded areas, corresponding to the three opaque black strips and four faded areas, each divided into five 1-inch squares which have each received different amounts of light. By placing sheets of different printing inks of the same color in the frame and exposing to sunlight to the same photometer number, the relative permanency of the different inks can be seen at a glance.

The photographic photometer may be bought at any photographic supply house which sells to professional photographers. If desired, three inks may be tested at one time by cutting the printed flat tints into strips 2 inches wide and 5 inches long and placing them in the frame so that each has an exposed and an unexposed area.

V. SPECIAL TESTS

The foregoing tests cover practically all the important components of the common inks. A few other tests might be made in case of trouble that can not otherwise be located.

Volatile constituents in the ink can be determined by placing a weighed quantity in a shallow layer in a porcelain or glass dish and heating in an air bath for one hour at 105° C, cooling in a desiccator, and weighing. It is hardly necessary to take the precaution of drying in an inert atmosphere. These volatile constituents may be benzine, turpentine, benzene, etc.

Certain patents call for the use of sodium silicate (water glass) in the thickening of the oil. The alkaline nature of this substance would prohibit its use in the presence of blue dyes and Prussian blue. It will probably be found with the pigment, and is easily tested for by treating the pigment with boiling water, filtering off the undissolved material, and testing the filtrate with phenolphthalein. It can hardly be considered a desirable substance in printing inks.

VI. ACCURACY OF THE ANALYSIS

While it may be assumed that every analyst desires to work with the greatest accuracy, frequently this must be sacrificed to some extent in order to obtain results in the shortest practicable time.

The foregoing analytical procedure has been in use in this Bureau for several years, and the accuracy obtained has been 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. That this is true of the analysis of printing ink is shown by the following statement, which shows how closely one may expect duplicate determinations to check:

Analysis of ink:
Oil and pigment separation............ 0.5–1 per cent of the ink.
Ash of ink........................... 0.1 per cent of the ink.
Oil analysis:
Unsaponifiable matter................ 0.2–1.0 per cent of the oil.
Rosin (i. e., the true rosin acids)....... 0.5 per cent of the oil.
Analysis of pigment:
Prussian blue........................ 0.5 per cent of the pigment.
Analysis of ash:
Determination of lead, iron, manganese.. 0.5–1.0 per cent of the ash.

It should be remembered that these figures would be materially less if calculated on the basis of the entire ink. For example, an error of 0.5 per cent in determining any of the constituents of the pigment would be only 0.1 to 0.2 per cent of the ink; 1 per cent of the ash would be from 0.02 to 0.1 per cent of the ink; and such accuracy is frequently more than is needed to judge of the quality of the ink. Probably a considerable part of the error is due to segregation, and the resultant difficulty in obtaining a true average sample.

VII. CONCLUSION

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