

draining and titrating direct in presence of the filter paper pointed out.

(4) In estimating the ferrocyanide in the residues obtained after extraction of spent oxide of iron with carbon bisulphide it is shown that a higher result is obtained if the alkaline solution be boiled and filtered before proceeding with the estimation. On boiling, some dissolved iron is precipitated which would otherwise cause precipitation of ferrocyanide on acidification. Lastly, caustic soda does not extract the whole of the blue from oxide, there being some varying residue of blue which is difficultly soluble in caustic soda and is probably in the form of the calcium-iron double salt.

DISCUSSION.

The CHAIRMAN said the principal point in the paper was that in the estimation of ferrocyanides on a large scale, that was in working up spent oxide of iron and other cyaniferous residues, certain losses occurred. He had known the Feld method to be used in gas works for estimating the cyanogen in the muds and raw products obtained by washing gas. It was unexpected both to Dr. Skirrow and himself to find certain discrepancies had crept in. He noticed that Dr. Colman had not mentioned them in his paper. The method for the decomposition of ferrocyanides into mercuric cyanide and then into hydrocyanic acid was interesting in that it had been used on a commercial scale. To his mind the zinc test was the most useful for cyanide works inasmuch as it could be used in the presence of impurities like sulphides and thiosulphates which would make the application of the copper test impossible. The sulphate of the alkaline metal had no effect if the solution were allowed to stand, and, that of course, was a point to remember in dealing with solutions that required titrating with zinc. There was also the influence of dilution. In experimenting on a large scale a difference of one per cent. was important in comparing a yield of say 80 or 90 per cent. with another yield of a similar amount. In the final results there would be a 10 per cent. difference, in the loss or gain which, of course, was a very big item.

Mr. J. H. HOSEASON enquired if Dr. Skirrow had further investigated the loss of the hydrocyanic acid in the first process. It seemed to him quite possible to break up the ferrocyanogen complex. It was possible for the hydrogen and cyanogen ions to take the other direction and be hydrolysed.

Mr. J. E. SOUTHCORRE said he had formed a similar idea to Mr. Hoseason with regard to the hydrolysis of the ferrocyanide. He believed it was possible during processes of hydrolysis for a great change to take place and cyanate to form. Cyanic acid was not volatile in steam, and, of course, that would account for the loss.

Dr. F. W. SKIRROW, in reply, said the one thing that had been brought out in Colman's work was the impossibility of titrating a solution of ferrocyanide either with copper or zinc, without reference to the alkali metal present. That was standardizing with the ferrocyanide of one alkali metal and titrating the ferrocyanide of another. It was clearly impossible to obtain accurate results in that way. He had not tried experiments with the copper salt. The advantage of being able to titrate in the presence of sulphites, sulphides, and thiosulphates, and so on, was so great that it had led him to confine himself to the zinc test. He had not gone into the question of the loss of the hydrocyanic acid, but he thought that hydrolysis would account for a great deal of it.

Scottish Section.

Meeting held at Glasgow, on Tuesday, January 18th, 1910.

MR. D. J. PLAYFAIR IN THE CHAIR.

THE FUNCTIONS OF STARCH IN THE MANUFACTURE OF PAPER.

BY JOHN TRAQUAIR.

In the manufacture of paper the most important factors in determining the quality of the finished products are:—

(1) The fibres, (2) the sizing agents. An unsized or waterleaf paper of even the finest quality is relatively soft and absorbent. It is also deficient in strength and cannot resist handling or mechanical wear and tear. The object of paper-sizing is to diminish the capillarity by cementing together single fibres, and at the present day two methods are in use, viz.:—engine-sizing and tub-sizing. Engine-sizing means rosin-alum-sizing, and for the specific ink and water resisting quality specially required in writing, printing, and wrapping papers, we are practically limited to rosin. It is not my intention to discuss this type of sizing at all, but papermakers know that it is the result of a complex process, influenced by quite a number of factors, and is not merely the simple process of adding substances of water resisting quality, which property they confer on the paper.

The other method (tub-sizing as it is called) deals with the finished sheet, and is a simpler process, colloid substances in solution, chiefly gelatin, being used. In this case the paper in the web or sheet is run through the colloid solution at a suitable temperature and concentration. The amount of size absorbed is regulated by the time of immersion, the nip or pressure on the squeezing rollers, viscosity of the size, and other factors. The paper is then dried at as low a temperature as possible by various methods. The colloid taken up by the paper coats the fibres, fills the interstices of the web with a structureless film, reduces the capillarity of the fibres, and the porosity of the paper.

This is the original method of sizing, and is at present universally used in high class papers for writing purposes.

Starch was the first paper-sizing agent, and it has been shown by Wiesner "Microscopical Examination of Paper," Vienna, 1887, that the European papers of the 8th to 14th century are exclusively starch sized, no rosin, gelatin, or tragacanth being present. A number of these papers can be written on with ink at the present day and are in excellent preservation. The art of sizing paper with starch seems to have disappeared from Europe in the 14th century and was replaced by animal sizing, and it is evident that the problem for the papermaker of to-day is to rediscover the lost art and apply it to modern conditions.

Regarding Asiatic papers, Wiesner in his "Eastern Turkestan (Chinese) Papers," Vienna, 1902, mentions a joint examination with Professor Karabacek of El Faijum papers with the following results:—(1) All the Faijum papers are sized with starch; other sizing agents such as rosin, gelatin, tragacanth, etc., could not be identified. (2) The majority can be written upon with ordinary ink to-day, after a lapse of 800 to 1000 years. (3) Unchanged wheat starch granules are frequently found along with inclusions of starch paste, gluten residues, and other constituents of flour, proving that in sizing there were used mixtures of raw and boiled starch, or half boiled starch. The presence of the gluten residues, etc., indicate that the purification of the starch was imperfect, or that an addition of flour was made in the sizing.

Karabacek "New Sources of Paper History," Vienna, 1888, gives extracts from an Arabian work dated 11th to 12th century, and entitled "The Scribes Assistant, or the Intellectual man's Equipment," as follows:—

1. "Now take the best sort of the finest and whitest flour and wheat starch, both purified. Soften and bruise the flour and wheat starch separately in cold water till no lumps remain. Pour on boiling water and stir, etc. Apply to paper by rubbing in, and dry in the air, etc." 2. Describes preparation of a solution of rice starch in which the paper is immersed, then dried and glazed. 3. Similar method to 2. in a manuscript 1701, but rice starch solution is spread on with a piece of linen cloth. The paper so treated is not distinguishable from genuine Bagdad paper. The ancient papyrus, according to Pliny, was treated with a plant sap to keep off moths and worms, and a starch paste prepared from fine flour with hot water and vinegar was used to join together the strips of which papyrus is composed. Pliny does not state how the sizing was done, but it is evident that hard sizing was not aimed at, as he says that polished or glazed paper does not absorb ink properly.

"Matthias Koops, Historical Account of substances used to describe events, etc.," 1801, states that:—"They (the Romans) sized papyrus in a similar method as we do rag paper, but they made their size of the finest flour which was stirred in boiling water with a few drops of vinegar and some leaven, and then filtered. It was after the first size beaten with a hammer; sized the second time, pressed and then smoothed." In Chinese and Japanese paper, rice flour is added to the pulp to fill up the pores and impart additional whiteness to the paper. These, however, are not hard sized; in fact, are frequently not sized at all.

In modern times the use of starch in papermaking is intimately related with the introduction and use of various vegetable fibres. Cotton and linen fibres were the earliest papermaking materials, and still produce the best paper, for in the raw state they exist as nearly pure cellulose, and therefore require little chemical treatment. The introduction of the Fourdrinier machine in 1803, and its subsequent improvements, was the means of putting papermaking in the way of achieving its present industrial importance.

The increased means of production stimulated the demand, and in fifty years, the paper made in the United Kingdom had increased from 11,000 tons (1800) to 63,000 tons (1850). As rags were almost exclusively the raw material used, a famine in rags threatened, and the search for new fibres began in earnest. In 1852 "esparto" was successfully introduced, and in a few years its use had far outgrown rags as a raw material. The repeal of the paper duty in 1860 and the introduction of chemical wood pulp in 1878 marked further periods in the progress of an industry whose growth has been one of phenomenal rapidity. In other fifty years the production of paper had multiplied itself ten times, the paper manufactured in the United Kingdom being 650,000 tons in 1900. At the present day, the consumption of the variety of products which can be classed as paper has reached such a figure and is increasing steadily at a rate which threatens destruction to the forests of the World.* This is so obvious that several of our large British paper consuming firms have within the last two or three years secured large forest areas, notably in Newfoundland with a view of ensuring for themselves future supplies of the chief raw material for their newspapers and other publications. Doubtless the ingenuity of our chemists will increase the number and sources of suitable papermaking fibres, and meet the increased demand in the future as in the past.

But to return to my subject, I said the use of starch was intimately connected with the introduction of the various vegetable fibres. The main facts are as follows:—It was found impossible to make a paper from esparto equal to a rag paper, and starch came into use as a necessary sizing and stiffening agent. It was about this time that the manufacture of starch on a large scale was started in this country, and the use of starch especially in Esparto E.S. writings and printings, grew to large proportions. In many cases the starch was used with little discrimination, and an entire lack of knowledge of how to get the best results from it.

After the introduction of chemical wood pulp, the use of starch steadily declined, the reason being that the hydrating capacity of this cellulose is at a maximum, and in use it added a wetness to the pulp, and a consequent hardness and rattle to the finished paper. Thus by combining esparto and well beaten chemical wood pulp a variety of results could be obtained, results in many cases very similar to those obtained by the use of starch, but there were other reasons for the decrease in the use of starch, among which we may mention (1) The gradual realisation by the papermakers that their methods of using starch involved a large loss. (2) Increasing competition and a consequent decreasing profit enforcing economy and thereby curtailing the use of starch. Not only so, but where starch requires to be used, the papermakers who formerly only used the finest starch now use cheaper qualities.

We now come to consider the function of starch in paper-making at the present day, and hope to throw some light

on the history of its use as briefly summarised in the preceding paragraph.

J. Hübner states (Cantor Lectures, 1903) "that it is quite safe to count it (starch) among the loading materials." This is news to starch makers if not to most papermakers, and I am afraid its price precludes its use for this purpose except in some special high class papers. The papermaker as a rule does not look upon starch as a loading or even a strength giver, but rather as a hardener and binder, influencing the feel, rattle, and retention of loadings. Starch may be added to the paper, either during its manufacture or as a final process. In the first case, it is added to the pulp in the beater, and is known as engine-sizing, and in the second case, it is applied as a surface size by a modification of the usual tub-sizing process.

The first method is the one in general use, and the starch performs various functions according to the class of paper in which it is used, the following being the principal classes:—

1. *Rosin size*.—A solution of starch is generally used to dilute down the rosin size before adding to the beater. The extent of dilution has a considerable effect on the efficiency of the size, and the presence of starch prevents precipitation of rosin on dilution and lessens the danger of having undissolved particles of sufficient dimensions to cause rosin specks on the paper. The starch colloid also assists in the distribution of the precipitated rosin compounds.

2. *Starch* is also used in special papers, such as cheque papers, where it is part of the test. (See Eng. Patent No. 748, Menzies and Bevan, 1891) as an example.

3. *E. S. Writings*.—Starch finds a much larger use in this class of paper, and in Scotland where the finest esparto E. S. writings are made, the use of starch cannot be dispensed with.

We have stated that the function of rosin-size is to add a water or ink-resisting quality to the paper, but it contributes little to the closing or compacting of the sheet. This effect is best and most commonly obtained by starch, but is, of course, also obtained by using other colloids, such as gelatin, casein, viscose, etc. The effect of adding a quantity of swollen or partly swollen starch to the pulp is the coating of the fibres with gelatinous starch hydrate. This adds a wetness or increased capacity for holding water, and as the water is longer retained in the passage of the pulp over the wire, the thorough interlacing of the fibre by the "shake" is assured. Under the action of the press rolls the interlocking of the fibres is favoured by the presence of a gelatinous substance which may be regarded as a kind of cement, and in the final drying the shrinkage of the now thoroughly swollen gelatinous starch, which accompanies dehydration considerably helps the process of compacting the sheet. It is this effect which justifies the use of starch, and although it can be obtained by prolonged heating and consequent hydration of the cellulose it is more economically obtained by starch.

4. *Imitation art*.—This is a class of paper which has come greatly into use within recent years, as it enables the printer to get very fair results with process block work on a paper which costs little more than an ordinary printing. It is therefore extensively used for magazines, catalogues, and periodicals, where the illustrations are not of first importance. In this class of paper, starch is used as a clay carrier, that is, its function is to fix the abnormally large proportion of china clay which is necessarily present in this paper. The finest imitation art paper is made in Scotland from esparto, and is loaded with from 25 to 35 per cent. of china clay, and as a final process is treated on the water doctor calendar where the sheet is alternately damped on the surface and hot calendared under heavy pressure.

The method of making paper depends on arranging the fibres in different planes, so that the surface consists of tiny hills and valleys, and calendaring consists in simply crushing down the hills into the hollows, so as to bring the whole surface into one plane. This is greatly facilitated by the alternate surface wetting and hot calendaring which also gives a polish to the paper.

Methods of using starch. Owing to the recent advance in the price of all starching materials, the time is most opportune for again considering the method of using starch in paper-making. At present it is added to the

* See Appendix (Census of Production, Table II, 1907) at end.

beater, and may be either raw, semi-swollen, boiled, or mixtures of these. The literature on the subject is very meagre, and the only scientific work on starch in its relation to paper is that by Alfred Lutz, *Papier-Zeit.*, 1908, 33 (This Journal, 1908, page 466). Unfortunately, this work was all done on the experimental scale, which rather discounts its value, but it shows the extent of loss in using starch under various conditions, and the experiments, although necessarily, carried out on hand-made papers, are strictly comparative. The amount of starch retained by the paper is found to depend mainly on the state in which it is added, although the nature of the starch and the condition of the pulp have minor influences.

In one series of experiments, 10 per cent. of starch was added to well beaten wood pulp, the yields being as follows:—

	Starch retained.		
	Potato.	Wheat.	Rice.
(a.) <i>Raw.</i>	per cent. 73.0	per cent. 71.7	per cent. 53.4
(b.) <i>Boiled.</i>	46.2	58.3	58.9

These results are very striking. In the raw starch experiments the per centage retained by the paper corresponds with the dimensions of the starch granule, and in the boiled starch experiments, to the fact that potato starch is relatively more soluble in boiling water. The extremely small granulated rice contains a much larger proportion of insoluble amylose which precipitates out on adding to cold water, the potato starch containing comparatively more soluble amylose. The increase in strength of the paper due to the addition of starch is proportional to the quantity taken up, and is fairly constant with different kinds of starch.

In order to determine the influence of starch on the retention of loading, a further series of experiments were done in which 5 per cent. starch calculated on the fibre was boiled to a paste with china clay and added to the pulp, comparative tests being done against pulp similarly loaded, but without starch.

	Clay retained.	
	Plain.	With starch.
Pulp with 5 per cent. rosin and 15 per cent. china clay ...	11.0	12.3
Pulp unsized with 50 per cent. clay	28.8	31.5

The additional quantity of loading retained by the starch does not compensate for extra cost, but without starch the paper was limp, and would have caused trouble on printing owing to dusting. This is prevented by the starch which imparted a feel and rattle to the paper. It was also found that the tensile strength and stretch of the paper was increased by 25 per cent.

On this question of retention of loading, the following facts from working scale experiments may be of interest. The clay was mixed with sufficient water and 10 per cent. of starch, and in one case the mixture was heated to fully 80° C., that is, the starch was thoroughly swollen. In the second case, the starch-clay-mixture was heated to 45–50° C., that is, the starch was not swollen, although a slight thickening took place. Equal quantities of these mixings were used in the same proportion of pulp, and worked separately on the papermaking machine. Average samples of the waste waters were examined for ash, which was also determined in the finished paper.

As a result, it was found that the waste water contained a larger quantity of suspended matter, and the paper a smaller percentage of ash when the starch had been thoroughly swollen, and that less suspended matter was contained in the waste water and a larger proportion of ash in the paper when the starch had only been heated to

under 50° C. Several experiments gave in every case similar results, there being on an average at least 25 per cent. more clay in the total solids from waste water in the case of swollen starch than with the unswollen experiments.

It is evident from the figures which have been quoted, that the best results are obtained by adding starch to the beater in a semi-swollen condition, that is, the starch should retain its natural granule form, being only slightly swollen and rendered plastic by the action of warm water. In this form the granules adhere easily between the fibres, stop up the pores, and at the same time bind the loading material. The raw starch does not adhere so readily, while starch paste, being practically a solution, is readily sucked or pressed through the pores between the fibres together with any particles of clay which may have settled in the latter. The swelling of the plastic starch granules is completed on the drying cylinder, and the maximum value possible by this method of using starch is obtained. In every case, however, it is evident that a loss of starch occurs, and 1 question if even under the best condition and a closed system of working, it is less than 33 per cent. of the starch used.

In the case of thoroughly swollen starch, we know it is much larger, although the full starching value is obtained for that proportion which is retained by the paper. In the case of raw or semi-swollen starch the drying cylinders are relied on to complete the swelling, but as the temperature of these is lowest at the wet end, the paper may be so dry by the time the temperature has been raised above the swelling point of the starch, that there is not sufficient moisture left to properly complete the swelling. This is very evident if a paper which has been engine sized with raw starch is carefully examined by the microscope. The paper should be torn so as to partially split it, then soaked in weak iodine solution to stain the starch and examined by say a 1 in. objective with reflected light. The starch granules on the surface will be swollen and diffused, but in the interior they are only slightly swollen and may retain their form so that the nature of the starch used can be easily identified. It is like ironing a collar too dry. It will lack stiffness owing to insufficient water being present to swell the starch granules. In this connection it might be worth mentioning that the modern, and by far the most economical laundry method of starching, is to use a thin boiling starch in which the collars are sized, then dried at a high temperature, damped, and ironed; the advantage being that every ounce of the starching or stiffening value of the starch used is obtained.

Now, the question occurred to me some years ago, why should similar methods of using starch not be applied in papermaking. This, of course, is reverting to the tub-sizing method, but after all, it is admitted on every hand that it is the best method of papersizing. The matter was discussed with a few papermakers and after many delays a paper making machine was altered to allow of these ideas being tested on a practical scale. A tub sizing trough was placed above the smoothers, and over this were several sparged cylinders, round which the sized paper travelled before being led on to the final drying cylinders.

I do not claim that this application was novel, but the idea was advanced with some appreciation of the difficulties to be overcome, and the knowledge that the first essential was to have a suitable starch product. The ideal product should yield a thin slightly viscous solution at 1½ to 2 lbs. per gallon, and give a tough flexible film on drying, as insoluble and unaffected by water as possible. Further, it must be produced at a price little above the equivalent of the starch ordinarily used.

The thin boiling maize and wheat starches now so extensively used in the large power laundries were first introduced and manufactured in America, and in Scotland at the Glenfield Starch Works, so that their properties and uses were quite familiar. Unfortunately, they are not quite suitable, as the solution at even 1 lb. per gallon sets on cooling, and when used hot "skins" easily and causes trouble unless a number of precautions are taken.

I have found that the starch esters, commercially known as "Peculose," (see this Journal, 1909, page 288), fulfil the conditions as to fluidity, permanency of solution, and

filming power. The film, however, is not insoluble, but the solution when treated with 2 to 3 per cent. of formaline and dried, gradually becomes practically insoluble, and much less water absorbent. These observations are still in the experimental stage, but similar results can be obtained by other means.

The end in view is the production of an improved printing surface, but the use of *Feculose* for tub-sizing, as usually understood may be dealt with first.

Tub-sized papers.—The makers of tub-sized paper have always viewed with suspicion any starch product which has been offered as a substitute for gelatin. The fact seems to have been entirely overlooked that the earliest papers were exclusively starch sized, and as far as sizing and durability are concerned are still unsurpassed.

All efforts to substitute a pure vegetable size for gelatin have ended in failure, and this fact has established the use of gelatin so firmly that tub-sizing has come to mean animal tub-sizing, and is frequently guaranteed as such. The advantage of *feculose* over animal size is that it can be dried at a high temperature and therefore more quickly, and the elaborate air-drying methods at present in vogue (and necessary where gelatin is used) can be largely dispensed with. No starch product, however, has the ink resisting power of gelatin, but this can be easily obviated by adding a little rosin-size to the *feculose* solution, and then just sufficient sulphate of alumina to decompose it. From 1—5 per cent. of rosin size may be used, and this gives the ink resisting quality. The *feculose* solution is distinctly colloidal in character, and does not penetrate the paper so readily as animal size. Comparative tests have shown that when used alone without alum the paper takes up the same amount of size from a 6 per cent. solution of gelatin as from a 12 per cent. solution of *feculose* at 90° F. Experiments run under these conditions on a papermaking machine where the half dried paper was run through the tub-sizing box, then over three-spurred cylinders, followed by ordinary cylinders and calendars, which dried and finished the paper in one operation, gave excellent results, the paper being in every way equal to that obtained by sizing with gelatin.

The fact that *feculose* does not give the tannic acid reaction has led to its use in conjunction with gelatin. This has opened quite a new field, and *feculose* is now in regular use in several works for tub-sizing paper. So far, its use has been confined to the cheaper class of machine made tub-sized papers; the makers of the higher class tub-sized papers being naturally very conservative. *Feculose* shows a 30 to 40 per cent. economy over gelatin, but in works where the gelatin is extracted directly, the difference is less.

A typical sizing bath is two parts 12½ per cent. solution of *feculose*, and one part 6½ per cent. solution of gelatin with just sufficient alum to give the required viscosity to the size. It has been found that *feculose* gives the paper a distinct quality, improving the handle by making it more pliable, and the writing quality by making the surface less hard and ink repellent.

E. S. writings.—*Feculose* is also used to improve engine sized writing, where the paper (which has been fully rosin-sized in the beater) when more than half dry is run through a weak solution of *feculose* and dried on the papermaking machine. The paper is tightly squeezed, so that little size is taken up, and it is endeavoured to keep this size as much as possible on the surface. This imparts the handle and writing quality of a tub-sized paper to an ordinary engine-sized writing, and leads to new outlets for this class of paper.

Printings.—In papers of this class the production of a good printing surface is the ultimate criterion of success. *Feculose* and china clay have been used in weak solution on the water doctor calendar with very promising results, but the conditions are rather difficult to adjust, and this use is at present in the experimental stage. Where the paper is tub-sized in *feculose* and colour, the conditions are more easily controlled, and encouraging results are obtained, the important point being that the loading is put where it is most required, viz., on the surface of the paper. Of course, under ordinary working conditions, you are limited to a very light coat, but the result is an improved printing

surface and the full value of every ounce of sizing material used is obtained on the paper. The china clay can be replaced by other colours, such as blane fixe, or satin white, with superior results, and as this paper has received what we might term a preliminary coating a much lighter final coat would be required if used as an enamelling paper. This opens a wide field of possibility, as the coating methods could be simplified, and the speed of coating greatly accelerated. The problem before papermakers to-day is the production of a printing surface which will take a process block at a price as near that of ordinary printings as possible. I feel sure the solution will be found on the lines I have indicated, but our experiments have not reached such a stage as to warrant a definite statement, although I will deal further with this under papercoating, where positive results have been obtained.

Papercoating.—This is a distinct branch of the paper trade, and in fact, forms a separate industry. The function of size, in this case, is to fix the mineral coating to the surface of the paper.

Few can have failed to notice within the last decade the enormous growth in numbers and circulation of illustrated papers. The better class periodicals have cultivated a popular taste for good illustrations and now no book or magazine is acceptable without them.

The development of modern printing paper is closely associated with the introduction of the photo-mechanical processes of illustrating. The application of photography and the designers' art to commercial purposes in the numerous monthly, weekly, and even daily papers, not to mention the numberless advertising pamphlets, catalogues, etc., has created a large and ever increasing demand for a cheap paper to give the most effective printing results. The wood engraving, the copper etching, the collotype, the lithograph, and the half tone process block, have each marked a stage in the advancement of the printer's art, and each required some special characteristics in the paper to obtain the best results. In the modern half tone block and three colour process work, a paper having a smooth surface is essential if a picture showing a sufficient amount of detail is to be produced. This smoothness of surface in the case of imitation art is secured by loading the paper heavily with china clay and water-finish on hot calendars, but if one will compare a picture printed from the same block on imitation art and on ordinary art enamel, it is evident why the former is called "imitation" art enamel. The picture in the former is very much inferior in depth and clearness, in fact, has a grey appearance.

It must be pointed out that the degree of surface smoothness should only be sufficient to take the maximum of detail possible in a process block, and the ideal position is arrived at when a paper with a surface just sufficiently perfect to take the maximum of detail possible is produced.

It must be confessed that the heavy highly polished art enamel which has been produced in response to the insistent, but often unreasonable demand, for something cheap, is not really paper. It is generally a sheet of poor vegetable fibres sandwiched between two coats of mineral matter which frequently amount to 50 per cent. of the whole.

The coating performs two functions: In the first place it fills up and levels the unevenness of the paper, and secondly it provides a printing surface. This is an important point and one that is generally overlooked by many paper manufacturers. It is the printing surface which is the essential condition. An imitation art enamel may have a perfectly smooth surface, and still give printing results very much inferior to a third or fourth class coated paper. The reason being, that the surface has no ink affinity; that is, it has no power of absorbing the ink from the block in the fraction of a second in which they are in contact; in fact, the surface is ink resistant, instead of being ink absorbent. The ideal coating for paper would be a solution of cellulose, but up to the present, although a number of attempts have been made, these have not proved successful. The manufacture of art enamel has been dealt with in a paper read before this Society by R. W. Sindall (see this J., 1905, page 770),

and I propose to confine my remarks to amplifying various points which were only briefly dealt with in his paper, and to deal specially with the application of starch, notably the starch ester or acetate feculose.

At first papercoating was all done by hand, the earliest machines being of the flat type, with round spreading brushes, which had a circular motion. In the early eighties the German cylinder machine was introduced with jigger brushes, and this has remained the standard type until the present day, although with a number of minor improvements. Some of the large art enamel firms have double coaters, but these are not completely successful, as the trouble of adjusting them scarcely compensates for the increased speed of production.

The paper used varies considerably, the best being pure esparto paper, then mixtures of esparto with chemical wood pulp in various proportions. In the cheaper qualities, mechanical wood pulp is used in increasing proportion. The pulp should be free beaten, and the paper as free from wire mark as possible, and little more than half rosin-sized. For good class chromos, it is essential that good quality body paper be used as this has a greater influence on the printing results than is generally credited. The colours used are of some interest.

(1). *Satin white*.—More of this colour is used than any other, as it possesses a maximum covering power combined with a high lustre. It is made by precipitating sulphate of alumina with excess of lime in fairly strong solution, thoroughly milling the precipitate, washing and filter pressing. The finished product therefore consists of a gelatinous alumina hydrate precipitate, calcium sulphate and excess of lime. I annex typical analysis which shows the composition of commercial satin white as used in paper coating. It should contain not more than 10 per cent. free lime.

Comparative covering powers show the following results. Method—Paint out on glass to equal density, the same weight of colour with one and a half times its weight of water.

	Area covered calc. to dry colour.	Price of pulp colour.	Average moisture.	Calc. price of dry colour.
Satin white	100	per ton. £4 10-£6	per cent. 65-75	per ton. £13 10-£18
Blanc fixe	50	£5 10-£7	25-30	£7-£9
China clay	35	£1 10-£2	5	£1 10-£2 5

Typical satin white.

	per cent.
Moisture	68-70
Al ₂ (OH) ₆	7-9
Ca(OH) ₂	6-8
CaSO ₄	13-17
Alkaline salts	4-6

A mode of comparative analysis might be mentioned. This may be termed Mechanical Analysis and consists in washing with water a weighed quantity of the satin white on a filter for several hours to remove sulphate and hydrate of lime. The insoluble consisting of alumina hydrate and the insoluble portion of the lime salts, this being examined for presence of china clay.

Results for 8 samples of at least 6 different makes.

	1	2	3	4	5	6	7	8
Moisture ..	64.3	67.3	70.2	70.2	66.5	73.7	70.4	66.9
Soluble extract	12.0	10.1	13.2	14.4	17.81	9.0	10.1	14.31
Insoluble residue ..	22.8	16.0	16.0	15.4	15.65	10.4	10.5	18.7

(2) *Blanc fixe*.—This is the next most important pigment, and is simply barium sulphate obtained by precipitating commercial barium chloride with sodium sulphate. It is usually sold as a white paste containing 25 to 30 per cent. moisture. An inferior blanc fixe obtained as a by-product in the manufacture of hydrogen peroxide is also on the market.

(3) *China clay*.—This is the well known mineral, and for paper coating good qualities are used. Cleanliness and good colour being essential.

Sizing material used :—(1) *Glue*.—The largest proportion of the paper coated in Britain is sized with glue, and for this purpose a good quality hide glue is essential. Special qualities are made for papercoating, and at least, 95 per cent. is continental.

(2) *Casein*.—This sizing material is a milk product obtained by precipitating separated milk with acid, washing, purifying, and then drying and grinding. A great deal more has been written on casein than on glue, or any adhesive substance, but the subject still presents difficulties with reference to the preparation of solutions, and mixture with other bodies, especially colouring matters. Casein was introduced as a size for papercoating in Britain in the year 1897, and made very little progress at first, as the method of making a solution was different from that employed with glue, which up to that time had been exclusively used for papercoating. However, the great economy effected, led some of the more enterprising papercoaters to take the matter up and solve the difficulties connected with its application with very satisfactory results. Casein is characterised by giving a very brilliant finish with satin white, and as the coat can be easily rendered absolutely insoluble by the use of formalin, it is particularly suitable for box enamels, and similar classes of paper. It also gives good results for process block printing in black and colours. On the Continent and in America, casein is used to a much larger extent than in Britain, and is undoubtedly unsurpassed for special classes of paper for decorative purposes. For some years the price of casein ranged from £20 to £25 per ton, but the price gradually began to rise owing to the use of the product in other industries and a general recognition that as a milk product it had a higher value if turned into cheese. In 1908 it had risen to over £30 per ton, while to-day its value is fully £40 per ton. At this price, its use as a size for paper coating is limited to the special class for paper for which it is peculiarly suitable.

(3). *Starch products*.—The fact that weight for weight starch has an equal, if not greater, sizing value than gelatin suggested its use in paper coating, and many attempts have been made from time to time to substitute a starch product for glue. The problem was to get a starch product which would yield a sufficiently fluid solution to make down the colour to a cream and still retain the original sizing power of the starch. Ordinary soluble starch was first tried in conjunction with gelatin, but many troubles were experienced, and it is questionable whether the economy is very real. At any rate, the use of soluble starch in this way is strictly limited. Soluble starch with 5 per cent. borax gives a solution which can be used for papercoating, but its sizing value is low.

It is recognised that unless a solution of the sizing material dries to a continuous film on glass, it is not suitable for papercoating. If it dries to a brittle mass, as is the case with ordinary soluble starch alone, or with borax, it will not give a continuous surface on paper. The broken surface will lead to considerable trouble in finishing, and will be absolutely fatal to the attainment of first class printing results. This has been my own experience, and is confirmed by the few firms who have experimented to any extent with soluble starch.

It is, however, possible to obtain a starch product capable of yielding a continuous film on glass and paper, and in 1900 a French soluble starch was introduced which fulfilled these conditions. This was manufactured by Brueder's process (see English Patent 17,650) August 16th, 1898, C. Brueder), and is an oxidised starch produced by the action of alkaline hypochlorites. Preliminary experiments gave encouraging results but subsequent tests on a manufacturing scale were not so successful, with the consequence that the prejudice which already existed against all starch products was further strengthened. It was found that a reaction took place between the alkaline satin white and the starch product, as the colour when freshly made up was all right, but in an hour or so the starch size became watery and lost its sizing power. Several attempts have been made to get a suitable starch product by an alkaline breakdown, but so far without success, as owing to the

treatment necessary to obtain sufficient fluidity the colour of the product is rendered unsuitable.

In 1901 I took up the problem, and confess to have spent seven years in solving it. In the first place, all the starch products on the market were examined as to their suitability, but without success, and my work was concentrated on the starch esters which at that time were simply in the laboratory stage. These esters have several ideal properties, fluidity, permanency of solution, good colour, and excellent sizing and spreading power, but in spite of this, for several years it looked as if the problem was to remain unsolved. Fortunately, I was in the position of having a papercoating work at my disposal, and was thus enabled to do experiments on a practical scale, in addition to laboratory work, and this fortunate combination must in some degree account for my ultimate success.

The various qualities of feculose (commercial starch esters) were tested as to their suitability. The main difficulties experienced were:—

(1) The setting of the feculose colour.

(2) Troubles on coating, grease spots, etc.

It was demanded that feculose size should be neutral, and remelt easily like gelatine, should it "set" or jelly on standing. The action of neutralising agents, such as borax, zinc oxide, magnesia, etc., were investigated, the result being that the neutralised feculose was of little merit as it set more quickly, and could not be remelted easily. The thickening action of borax, alumina and its salts was noted, but these reactions do not improve its papercoating quality. The usual remedies for spotting, such as the addition of a little oleine to the colour were tried, also other agents whose efficacy is a superstition among colour mixers, but these had only a harmful effect. Mixtures of feculose and other sizing agents were also investigated.

Feculose and casein do not mix, but feculose and glue can be used together, although the results did not justify the continuation of experiments in this direction. Owing to the successful application of mixtures of gelatin and feculose for tub-sizing, the matter was reopened at a later date. The best method is first to mix the colour with the proportion of feculose size and then add the glue size to complete the mixing. This development was thoroughly tested on a working scale, but the results were disappointing. The colour is apt to be frothy, and while fair results are obtained with light coats, heavier coats show pin holes and other imperfections. In mixtures of colloids with such distinct origin and properties as gelatin and feculose, separation occurs on standing, and until some knowledge of the constitution of those bodies is obtained, we can only hope to experiment on crudely empirical lines. Towards the end of 1905 a much cheaper type of feculose was tried, and while this gave excellent results with neutral colours (such as blanc fixe and china clay) it was a failure with satin white. A neutral or acid satin white was made and tested, the only point of interest being that with this colour a perfectly dull finish was obtained. The whole question finally resolved itself into the production of a starch product which would be unaffected by alkali, as far as its sizing properties are concerned.

All the types of feculose which had so far been tested reacted with alkali, the solution becoming thin and watery, except in one instance, which gave me a hint as to the direction in which a solution of the problem was to be found. After careful experiment, it was evident that any oxidised starch was acted on by alkali, and this was confirmed by some published work at that time. This cleared the way for further investigations, but it had taken four years to reach this point, although the work during these years had not been valueless. A new type of feculose was evolved to meet the requirements. The conversion is carried sufficiently far to give a product which yields a thin solution with four or five parts water, and keeps permanently fluid for several days. The product as discharged from the converter contains about 4 per cent. free acetic acid and 6 per cent. combined acetic acid, and in order to make it a marketable article the free acid has to be removed. At first this was neutralised by the addition of various alkalis, but very much better results were obtained from a washed product. At present it is

sent out in three forms: (1) As it comes from the converter, in which case, the papercoater prepares the feculose by washing by decantation, and then boiling as usual. (2) Hydrous feculose. This is the washed, but undried product, and is sent out in barrels in the pulp form containing 50 per cent. moisture. We find it keeps perfectly, and in this form it is prepared for use with a minimum of trouble. (3) The washed and dried variety. Feculose has now been used in such quantity that we can positively affirm that it meets all the requirements of a papercoating size. It is prepared for use by boiling, by any convenient method, with four or five times its weight of water. In mixing with the colour, if the chemical composition of feculose is borne in mind, no difficulties will arise. It is a partial starch acetate, containing 5 or 6 per cent. combined acetic acid, which on hydration produces an enormous effect on the starch complex for reasons which are as yet obscure. With neutral or acid colours, no reaction takes place, but with alkaline colours such as satin white, the starch acetate is slowly decomposed with regeneration of an insoluble starch hydrate. As heat accelerates all chemical reactions it is best to cool the feculose solution before mixing with the satin white, this retards the thickening which takes place, and the colour liquefies easily on warming up should it become rather thick.

It is this reaction which accounts for the excellent working properties of the feculose colour as it sets on the paper when spread out and exposed to the drying temperature, in which respect it is the direct opposite of animal size.

The feculose colour can be used right away as it comes from the mixer; is never frothy in working; can be dried at a higher temperature than glue, and therefore saves considerable time. Papercoating is a process of details, and it is quite impossible in this paper to deal with anything other than a few of the more important features.

Comparisons:—When compared against the finest hide glue, 15 to 20 per cent. more feculose is required to give an equally hard sized surface, the figure for the best quality casein being very similar.

Finishing:—Under equal conditions with satin white the finish is practically the same as that obtained with glue, but not so bright as with casein. It must be recognised however that in using starch products the usual laundry methods of obtaining a high finish, must to a certain extent be adopted, i.e., calender the slightly damped surface with a hot calender, and heavy pressure.

Printing:—The feculose surface has an unique ink affinity with the remarkable property of quickly taking up the ink from the stone or block, enabling it to give under comparative conditions printing results unequalled for density and solidity of colour. This quality of the feculose paper has to be recognised, and it sometimes suffers from the defects of its good qualities. This ink affinity can be modified to any extent by the addition of a little rosin size to the colour.

Owing to feculose being a starch product, it can be dried at a high temperature without its sizing power being affected, or the size drying into the paper as occurs with glue, and this property opens a wide field of possibility for the simplification of the present drying process, which is universally some type of festooning.

With the view of simplifying the present process a series of experiments were done some years ago. The paper was coated on an ordinary surfacing machine with the size alone at different concentrations, and then with varying proportions of (1) china clay, (2) Blanc fixe, and (3) satin white. The results were interesting. The size alone gave imperfect prints, the surface, although smooth, was absolutely ink resistant, and the ink took several days to dry. With china clay, better results were obtained, and still better with blanc fixe, in every case, the printing result improved with the increase of mineral matter, up to, of course, the fixing limits of the size. With satin white, however, the best results were obtained, the difference being very marked with light coats. The satin white surface had the highest finish, and the peculiar ink affinity, the whole series demonstrating in a very striking manner that it is the surface with the proper ink attraction that gives the best results under ordinary printing conditions

This has been pursued further, and it has been demonstrated that a paper with a coat of only $7\frac{1}{2}$ grammes per square metre (3 lb. per ream D.C. 480s.) will give printing results equal to an ordinary chromo with a coating of 30 to 40 grammes per square metre (12 to 16 lb. per ream D.C. 480s.). The paper used need not cost any more than an ordinary enamelling, but is preferably surface sized on the papermaking machine with feculose alone, or an admixture with some china clay to fill up and harden the surface. With coats of under 10 grammes per square metre, the paper can be treated at the full machine width, and dried over cylinders at a high speed, the production by this method being enormously greater than by the usual festooning process, where you are limited to 30 ins. or 40 ins. width. The process is still in embryo, but the results up to date have demonstrated its possibilities (see English Patent No. 16,327, 1908. S. Milne). This paper has the merit of durability, as it is mainly fibre, and does not show fully 60 per cent. ash, as is the case with many art enamels.

STATISTICS.

The papercoating industry is distributed very evenly between England and Scotland, there being seven firms in each country who are papermakers and coaters. It does not follow that the paper used for coating is their own manufacture, as in several cases a large proportion of the enamelling paper is bought from other firms who make a speciality of this class. These 14 firms control 80 one-sided coating machines, and of these 60 will run 24 hours per day. There are also eight double-coating machines in regular use, which equal 16 ordinary coating machines. There are 10 firms of papercoaters who are not paper manufacturers, controlling 70 surfacing machines and about 10 board coating machines. These all run 10 hours per day, and turn out a variety of work. There are also one or two large printing firms who have a papercoating department.

There are produced in Britain about 20,000 reams of art enamel per week, and 15,000 reams of chromo and other coated papers. This requires fully 50 tons per week of sizing material, which at present, is mainly glue of Continental origin.

Finally, there is one striking fact regarding this industry which impresses anyone who has had the opportunity of intimately studying the general conditions—viz., the absolute lack of any scientific control.

This militates against the introduction of improved methods, stifles experimental work, and frequently leads to other exerecences of which the least said the better.

In conclusion I have to thank several friends in the paper trade for their criticisms and suggestions, and particularly Messrs. Wm. Wotherspoon & Co., Glenfield Starch Works, Paisley, for permission to publish the foregoing paper.

APPENDIX.

(Census of Production, 1907.)

TABLE I.—OUTPUT.

Note.—The figures in this Table are given to the nearest thousand in each case. Amounts lower than five hundred are not shown.

	England and Wales and Ireland.	Scotland.	United Kingdom.
	Quantity.		
Paper:—	Cwts.	Cwts.	Cwts.
Paper for Writing and Drawing and for Envelopes	1,145,000	1,340,000	2,485,000
Paper for Printing and for Posters, &c.	7,601,000	1,000,000	8,721,000
Packing and Wrapping Paper, Biscaps, &c.	3,024,000	613,000	3,637,000
Printed and Coated Papers (not Hangings)	315,000	306,000	681,000
Pasteboard, Cardboard and Millboard	749,000	144,000	893,000
Other Sorts	424,000	140,000	564,000
Paper Bags	551,000	159,000	710,000
All other Products	17,691,000		
	Recorded by value only.		
	Tons.		
	=884,560		

TABLE I.—continued.

	England and Wales and Ireland.	Scotland.	United Kingdom.
	Value.		
	£	£	£
Paper:—			
Paper for Writing and Drawing and for Envelopes	1,591,000	1,404,000	3,085,000
Paper for Printing and for Posters, &c.	4,703,000	887,000	5,590,000
Packing and Wrapping Paper, Biscaps, &c.	1,570,000	373,000	1,943,000
Printed and Coated Papers (not Hangings)	389,000	457,000	846,000
Pasteboard, Cardboard, and Millboard	455,000	110,000	565,000
Other Sorts	538,000	102,000	700,000
Paper Bags	391,000	96,000	487,000
All other Products	92,000	20,000	112,000
Total Value	9,729,000	3,599,000	13,328,000
Total Value for England and Wales	9,554,000	—	—
Total Value for Ireland	175,000	—	—

TABLE II.—COST OF MATERIALS USED, SHOWN IN RELATION TO THE VALUE OF OUTPUT.

Note.—The figures in this Table are given to the nearest thousand in each case.

	England and Wales and Ireland.	Scotland.	United Kingdom.
	£	£	£
I. Cost of Materials used	6,411,000	2,405,000	8,816,000
II. Value of Output	9,729,000	3,599,000	13,328,000
III. Value of Output less Cost of Materials used	3,318,000	1,194,000	4,512,000

Yorkshire Section.

Meeting held at Queen's Hotel, Leeds, on Monday, February 21st, 1910.

LORD ALLERTON IN THE CHAIR.

PROBLEMS OF THE LEATHER INDUSTRY.

BY PROF. H. R. PROCTER.

Though the technology of leather manufacture is one of the most ancient, and has been highly developed by the accumulated experience of ages, it is as yet less influenced by scientific knowledge than many other industries. This is less due to any special ignorance or unwillingness of tanners than to the extraordinary difficulties of the problems it presents, and the risk and costliness of experiment. Much has, however, been accomplished in recent years towards clearing up the prevailing darkness, and this has been hastened by the introduction of new tanning agents, such as chrome salts and aldehydes, which are so far removed from the older methods as to render much of the previous experience valueless, and to compel the adoption of new methods and a study of their underlying principles.

The skins of animals naturally presented themselves to our forefathers as valuable for clothing and other purposes; but, wet, they were subject to rapid and offensive decay, while, dried, they became hard and horny; and therefore