THE ACID ACTION OF DRAWING PAPERS.

BY C. P. CROSS AND E. J. BEVAN.

Is a recent communication to the Chemical Society (Proc. Chem. Soc. 1892, 19) Professor W. N. Hartley has called attention to the "acid action" of drawing papers. After examining representative specimens—chiefly "Whatman" papers—he arrives at the following conclusions:—

1. That the majority of papers of this class show an acid reaction. 2. That the acid reaction is due to the presence of free acid. 3. That this acid is sulphuric acid left in the "fibre" (rags) through imperfect washing after the process of souring. 4. That this conclusion from the results of analysis is supported by the observation of the difficulty of removing sulphuric acid from linen fibre by successive and exhaustive treatments with pure water.

It would occur to anyone familiar with the technology of paper-making that Professor Hartley was unaware that the details of manufacture render his conclusions in the highest degree improbable, and that therefore the evidence upon which they are based should have been proportionately unimpeachable.

To these conclusions, taken in order, we will oppose the results of our own experience in regard to these papers, which afford a much simpler and, *a priori*, more probable explanation of the acidity which Professor Hartley has observed.

1. The reactions of these papers, if and when acid to certain indicators, such as those employed by Professor Hartley, are *basic* to others, e.g., methyl orange and Congo red. 2. That the apparent "acidity" is due to the presence of a *basic sulphate of alumina*, alum being an essential constituent of the mixture used in sizing these papers. 3. That in the making of the "Whatman" papers no free acid could survive the long process of washing of the soured rags. They are in fact treated for 3 to 4 hours in an "engine" with a continuous stream of the *exceptionally hard water* of the district (Maidstone). 4. In the "Whatman" papers *cotton* and not *linen* (flax) cellulose is the preponderating constituent.

To bring the matter, however, to a more direct experimental issue we procured samples of the following makes of "Whatman" paper, which were submitted to examination:—

1. Imperial.....	140 lb.	1891.
2. Imperial.....	72 lb.	1892.
3. Imperial.....	96 lb.	1892.
4. Double Elephant	133 lb.	1892.

These papers all showed a distinctly acid reaction with litmus and cochineal. The aqueous extracts from weighed quantities of the papers were titrated with standard alkali in presence of litmus as indicator; the results are given below, calculated to 100 grms. of the papers:—

1. Required to neutralise	1.3 cc. normal NaOH
2. " "	2.3 cc. "
3. " "	1.3 cc. "
4. " "	4.3 cc. "

With carefully neutralised solutions of Congo red and methyl orange on the other hand, the papers, as well as the aqueous extracts, gave a distinctly *basic* reaction.

Analysis of the aqueous extracts showed that they contained in each case a *basic sulphate of alumina*, and estimations of alumina showed that the quantities present were approximately in the ratio of the above results of titration.

Papers (1) and (4) were further treated with pure absolute alcohol. After evaporating the alcohol, the residues were treated with water, and the solutions, *basic to methyl orange*, were titrated with standard acid. Calculating the results on 100 grms. paper:—

1. Required to neutralise	0.6 cc. normal acid.
4. " "	0.5 cc. "

It is sufficiently proved by these results that *the papers do not contain free acid*; on the other hand, that they do

contain sulphate of alumina, but in the form of a *basic salt* with a ratio $\text{SO}_3 : \text{Al}_2\text{O}_3$; *certainly less than 5:2*. (Compare this Journal, 1886, 73; 1889, 253.)

We do not deny of course that papers *may* contain free acid, and it is not for us to say that the papers examined by Professor Hartley did not contain free acid. What is certain, however, and what we desire to emphasise, is that the *evidence* adduced by him being merely that of an *acid reaction*, is no proof whatever of the presence of free acid. We now suggest the only probable explanation consistent with the experience* of specialists, and with the results of examination of fair, trade samples of the particular papers which he has found to possess the serious defect in question, and Professor Hartley will no doubt take this suggestion into consideration in any further investigations on this subject.

We may now look a little more generally at the important questions opened up by the communication which we have found it necessary thus to criticise.

1st. Is the "acidity" of a sulphate of alumina more or less *basic*—which we take to represent a normal acidity of hard-sized papers—prejudicial to the permanence of pigments applied in the form of water colours to the paper containing this salt? The answer to this must come from those who have made a special study of pigments in relation to the conditions under which they have to struggle, so to speak, to retain their beauty unimpaired.

2ndly. Admitting for the moment that the condition of "acidity" does prejudice the life of pigments, is it in the power of the paper maker to suppress this acidity without prejudicing on the other hand the quality of his paper *quâ* paper?

To this question we can give an answer based upon experience. Most of the high-class papers made in the Kentish district are finished with a neutral or slightly basic reaction. There is every reason, *a priori*, why this should be so. The souring of bleached rags is an exceptional treatment, and, this excluded, the treatment which the rags undergo, i.e., boiling and bleaching, are uniformly with alkaline or basic reagents. The alum of the size is then the only contributor of acid, and to its action is opposed, in addition to the basic residues from the above treatments, that of the exceptionally hard waters (14–20 grms. CaCO_3 per gallon) used in the manufacture—and we may reckon at the very lowest 5,000 gals. per ton of paper used on the machine—and also that of the soap, which is a usual ingredient of the mixture used in sizing.

Thus at Messrs. Joynton's mills, St. Mary Cray, where the process of souring the rags is seldom resorted to, the papers produced, including the drawing paper, finish with a neutral or slightly basic (to litmus) reaction.

At Messrs. Balston's mill, where the "Whatman" papers are made, the souring process is practised; but the condition of the subsequent treatments are so adjusted that the alum used in the sizing is reduced to the condition of a *basic sulphate* in the finished paper.

Our final conclusions are therefore these—

(1.) The "acidity" of drawing and other papers—when normally acid—is not due to the presence of *free acid*, but to sulphate of alumina, always more or less "basic," but with reactions which are acid to certain indicators.

(2.) That if shown to be a defect in relation to any uses for which the papers are intended, the acidity may be suppressed by the adoption of very simple expedients, without prejudice to the qualities of the papers.

DISCUSSION.

Mr. Wm. THORP had not heard the original paper, and therefore was not fully informed on the subject. His experience had been that it was easier to get chemicals into fibres than to get them out. He had first encountered the question in the case of water analysis some years ago, when it had been necessary to free filter-paper from ammonium. He had passed many litres of water, free from

* The sum of the evidence adduced by Professor Hartley is the acid reaction *together with* precipitation of BaSO_4 in adding BaCl_2 to the aqueous extract. The *a priori* interpretation of this evidence should have been the presence of a sulphate having acid reactions.

ammonia, through a filter, and the ammonia was present in the filtrate to the end of the chapter. That led him to the conclusion that the ammonia was present inside the fibre of the paper, and required time for removal. The difficulty was overcome by soaking the filters for some days in water free from ammonia, then, on using them without drying, they imparted no ammonia to the filtrate. His remarks were made, not so much as a criticism of the paper, but as a hint to those present as to the difficulty of removing soluble substances from fibres.

Dr. SAMUEL RIDEAL thought that the authors' statements came rather late in the day. He was under the impression that the last numbers of the *Chemical News* and *Proceedings* of the Chemical Society contained a paper by another author, who stated that the presence of sulphuric acid was probably due to alum being present in the fibre of the paper. There was one point which had not been raised by the authors, and which was mentioned in the discussion on the original paper by Professor Hartley, namely, whether it might not have been possible that the papers had absorbed sulphuric acid from the air. That would exonerate the manufacturers, but at the same time render it possible for sulphuric acid to be present. He had been offered a sample of Whatman's paper, made in 1837, and he would be very glad to present it to the authors of the paper if it could be of any use to them.

Mr. JOSEPH ARNOLD, as a manufacturer of one of the papers mentioned, would like to state that no acid whatever had been used in the manufacture of his papers, they were simply made of linen and cotton rags washed in pure water, no acid, chlorine, or chemical of any kind being used. He could not, therefore, understand how Professor Hartley could find acid in his (Mr. Arnold's) paper.

Mr. W. F. ANDERSON, as one who had had a wide experience in making drawings, would like to say that he was always under the impression that drawing paper was made of linen, and cartridge paper of cotton. There was a very great difference between proper drawing paper and cartridge paper. He had known the size to disappear from the paper, and had in fact found that a roll of drawing paper invariably got spongy after 12 months, owing to that cause. Those who were makers of drawing paper would do well to look into that point. He did not know what the paper mentioned by Dr. Rideal made in 1837 could be. If he was right in his suspicions, it would be little better than blotting paper now.

Dr. RIDEAL thought it would be interesting to see whether the paper referred to contained any alum, *i.e.*, whether the sizing had been rendered antiseptic by the addition of alum. As the paper referred to had been exposed in a stable for 20 years, any sulphuric acid which might have been present would probably be found as ammonium sulphate.

Mr. H. GALLON explained that the reason why paper became spongy was that it was not kept properly. Paper was a most delicate substance to keep in working order, and after a few years the size would be affected by damp, and sponginess and spottiness would ensue.

Mr. BEVAN, in reply, said that with reference to Mr. Thorp's observation as to the difficulty of removing chemicals from fibre, he would like to point out that this difficulty chiefly applied to solutions of an alkaline nature. It was well known that it was extremely hard to remove caustic soda from cellulose, but it was a simple matter with acid. The process to which rags were subjected was much more drastic than any laboratory treatment. The rags were broken up until they formed almost a milk in the water. Referring to Dr. Rideal's remarks as to the possibility of the paper being acid on account of the action of sulphurous acid derived from coal-gas, if the facts were as he (Dr. Rideal) had stated, Professor Hartley ought to set the matter right, so as to exonerate the paper-maker. He (Mr. Bevan) presumed that Mr. Arnold's statement that no chemicals were used in the manufacture of his paper referred to the first treatment of the rags. He supposed

Mr. Arnold would not wish it to be understood that no chemicals were used in the sizing. (Mr. Arnold remarked that chemicals were used in the sizing.) He (Mr. Bevan) would point out that certain makes of paper, such as Joynson's, not only contained no free acid, but actually gave a slightly alkaline action to certain reagents.

EXPLOSIVE NITRATES FROM THE JUTE FIBRE.

By C. F. CROSS AND E. J. BEVAN.

In a recent issue of *Dingl. Polyt. J.* **283**, 88, we read a communication by Otto Mülhåuser under the title, "Die Jute ein Rohstoff für Schiesswolle."

Following the appearance of this communication, we observe that the journal "*Industries*," 1892, 236, gives prominence to an abstract of the author's results under the title, "Nitrojute, a New Explosive."

Those who have studied the chemistry and chemical technology of the jute fibre will, with ourselves, be anxious to discover what Dr. Mülhåuser has contributed to the advance of either, or both.* The substance of the communication in question we take to be the quantitative study of some four preparations of the well-known explosive nitrates obtainable from this fibre. The conditions of "nitration" chosen were a comparatively long immersion in the nitrating acid, the composition of which (ratio $\text{H}_2\text{SO}_4 : \text{HNO}_3$) was varied, as was also the proportion of acid to fibre. With the long exposure (3—4 hours) to the nitrating acid, there is, as the author states, a disintegration of the fibre bundles, and the nitration is attended by secondary decomposition and conversion into products soluble in the acid mixtures. These facts were fully described by ourselves some few years ago (*Chem. Soc. J.* **55**, 202), and from them we concluded that the highest yield of nitrate is represented by an increase of weight of 55 per cent., corresponding approximately with the formation of a tetranitrate of the *ligno-cellulose*, which latter we formulate for statistical purposes as $\text{C}_{12}\text{H}_{13}\text{O}_7$. In this product the general structural features of the original fibres are preserved. This high yield is only obtained with exposures of short duration: in fact, after 15 minutes' immersion at the ordinary temperature, decomposition is usually seen to ensue with liberation of gas and the appearance of nitrous fumes.

In Mülhåuser's experiments it is evident, from the conditions of the treatment and from the low yield of the products (130 per cent.), and from the disintegration of the fibre bundles, that such secondary decompositions took place, and that the products probably, therefore, approximate to derivatives of *cellulose* rather than of the *ligno-cellulose*, the more oxidisable "non-cellulose" or lignono constituents having suffered decomposition.

The author, in fact, regards his product as a *cellulose* pentanitrate— $\text{C}_{12}\text{H}_{13}\text{O}_5(\text{ONO}_2)_5$, but appears to consider it unnecessary to account for the intermediate steps by which such a product has been obtained from a compound cellulose (of the approximate formula $n.\text{C}_{12}\text{H}_{13}\text{O}_5$). We have suggested the above explanation on the basis of our own researches, and hope that it may receive due consideration in any further investigations which the author may carry out on the subject.

From the point of view of technological application, we have always failed to see any advantage in the lignified textile fibres as raw materials for explosive nitrates.

There are a large number of raw materials approximating more or less to a pure cellulose which can be obtained at from 10*l.* to 25*l.* a ton, and which will yield on treatment from 150 to 170 per cent. of explosive nitrate, superior in explosive power and stability to the products obtainable from jute *et similia*. In our opinion, therefore, the application of the latter is not within the range of practical consideration.

* Dr. Mülhåuser's views of the constitution of the jute fibre as a chemical individual are hardly reconcilable with our own (*Chem. Soc. J.* 1880, 608; 1892, 90; 1899, 199; *Chem. News*, 77).