

depends essentially on the presence of the sensitizers under consideration.

Now, up to the present, it has not been found possible to make a collodion emulsion of equal sensitiveness with one of gelatine, either by means of long-continued cooking or by the addition of ammonia. This fact can be explained by reference to the different modifications to which silver bromide is subject, according to the investigations of Stas. The eminent Belgian chemist has described a highly sensitive form of the bromide of silver produced by continuous boiling of the salt in water for many days together. It is so sensitive that exposure to the flame of a Bunsen burner for a couple of seconds is sufficient to produce blackening, and so finely divided that it remains suspended in water. Similar to the effect of boiling in water, as stated by Stas, is the long-continued stewing of the gelatine emulsion. Now, cooking a collodion emulsion has not the same beneficial effect, but this is due to the fact that, in this combination, the silver bromide exists in another and denser condition, which cannot be changed to the finely-divided modification of Stas. That such conditions really exist has been proved by Dr. Szekely; he precipitated bromide of silver from an aqueous solution containing glycerine, according to Abney's formula, washed it, and then emulsified it by stewing it with gelatine. By this process he obtained a very uniform emulsion, which had about the same sensitiveness as that of wet plates and which was not rendered more sensitive by cooking for several days.

It thus appears that the bromide precipitated from an aqueous solution has different properties from that produced by precipitation in gelatine. Similar properties, however, are apparently possessed by silver bromide precipitated in an alcoholic solution. Silver nitrate is known to be very scarcely soluble in alcohol, and the small amount dissolved in that liquid has the tendency, especially in the presence of ether, to become insoluble and to precipitate in tolerably large particles. No wonder, then, that the silver bromide precipitated from such a solution should be thrown down in a denser condition than is the case in an aqueous solution. Owing to this state of density, the decomposition of salt by the action of light, and by that of the developer, is hindered, and thus may be explained the want of sensitiveness. Personally I feel sure that, by some contrivance, it will be made possible to obtain the silver bromide in a finely-divided condition, and to incorporate it with the collodion.\*

We come now to another point for consideration, namely, the color of the bromide. Stas states that the finely-divided pearl-white bromide of silver is immediately turned to a deep yellow color on contact with ammonium bromide. This change of color goes hand in hand with the absorption of light, and only that kind of light which is absorbed acts chemically on the silver bromide. Now, since yellow bromide of silver absorbs blue light much more powerfully than white, it will also exhibit greater sensitiveness to the blue rays. In this way the physical properties of silver bromide may have an effect on its sensitiveness. There is, however, the condition that the salt must remain in a finely-divided state. Should the bromide, when it assumes the yellow modification, be rendered coarser in grain, its facility for reduction of development will be lessened, and for this reason its sensitiveness will be affected.

There is still a point to be considered: gelatine which has become partially decomposed by long cooking acts appreciably as a sensitizer. Dr. Lohse has observed that, when gelatine alone is cooked for a long time and then used for making an emulsion, the latter is found to be very sensitive.†

In the experiment of Dr. Szekely above described, it must be confessed this sensitizing power of the gelatine has no effect; this, however, is caused by the silver bromide being present in a coarser state; and, according to Dr. Eder's observation, it will not be rendered finer, but rather coarser, by longer continued heating.

The longer the gelatine emulsion is cooked the greater will be the quantity of the products of decomposition; and it seems to be highly probable that these products, like all the results of spontaneous decomposition of organic matter, have a reducing action. There is also another cause: both Dr. Eder and Dr. Lohse have proved that ammonia is formed when a solution of gelatine is kept hot for a long period of time. Now, when ammonia comes into contact with a substance capable of reduction, it acts as an alkaline developer, that is, in this case it reduces the bromide of silver. It is well-known that even silver bromide which has never been exposed to the light is gradually attacked by an alkaline developer. Hence also it arises that, after very long-continued emulsification, an emulsion will give plates liable to fog.

Berlin, April 1, 1880.

#### EXPANSION OF PAPER.

It is tolerably well known to most persons that paper when wetted expands, and also that it contracts again when dried; but it is not so well known to many that its expansion is always greater in one direction than in the other. Thus, if a sheet of paper be cut exactly square and then wetted, it will be found to measure more in one way than it will in another. This property often gives rise to difficulties when mounting prints that have to be joined or matched in size.

Some few years back we published in our pages the fact that a photograph printed on paper cut from the sheet in one direction would, when mounted, be of a different size from a print cut the other way, although both were printed from the same negative; that is, prints made on paper cut lengthwise from the sheet will, when wet, be of a different size to those made on it when cut crosswise. Therefore, it will be found impossible to match them accurately when they have to be joined in mounting, which is frequently necessary.

With a view to elucidate this matter further we have recently made a series of experiments with a number of different samples of paper, selecting only such as are employed in photography either for silver or carbon printing. It is to the latter process that the importance of this subject is the greatest, inasmuch as it is now more extensively employed for large work than the former, and, consequently, on account of the size, any variation will be more manifest. We may here state that nearly all papers now in the market—certainly all those used in photography—are made in continuous lengths, to be afterwards cut up into sheets of

the requisite size. It becomes important, therefore, to know which way the sheet is cut from the roll—whether longitudinally or transversely; for, as we shall presently show, upon that depends the amount of expansion.

The first paper we experimented upon was thick Saxe. This paper is made in continuous lengths of half a mile or more, and about fifty-five inches wide. This width allows of three sheets, eighteen inches wide, being cut, and the edges of the outer sheets trimmed off. The water-mark, "Steinbach, Malmédy," appears at short intervals down both edges of the web, so that it may always be known which way the sheet was cut by looking for the water-mark. This, of course, will not be seen on those sheets that are cut from the middle, but it may always be assumed that the longest way of the sheets are cut lengthwise from the roll. Two strips of exactly twenty-four inches in length were taken, the one cut lengthwise and the other crosswise of the web. They were soaked in cold water for half an hour, then laid very carefully on a sheet of glass and measured, and it was found that the strip cut across measured twenty-four inches and three-eighths, while that cut lengthwise was a quarter of an inch less, showing that it had expanded only to the extent of one-eighth of an inch, and the other had to three-eighths.

The same experiment was repeated with different kinds of paper, such as those employed for transfer paper in carbon printing. One of these was a very fine sample of paper of foreign manufacture and very close in texture. This did not expand in any appreciable degree in the length, while in the width it did to the extent of a full quarter of an inch. Another sample—a commoner variety, although a paper of good quality and of home manufacture—did not expand any more than the previous one did in length, although it did to the extent of three-eighths in width.

Two other samples—both of a very hard and close texture—were next tried, and they were found not to expand at all in the direction of length, and only a quarter of an inch in width. Each of the above samples could be stretched considerably without breaking, the Saxe most of all, doubtless on account of the long fiber of the pulp of which it was made.

All the strips were placed in warm water for the purpose of seeing if that would make any material difference in the expansive property; and we found that it did, for after a quarter of an hour's soaking each of the pieces that had been cut transversely from the web in each instance had lengthened an eighth of an inch more, although those cut longitudinally were in no way affected. We noticed, however, that in all cases the paper could be stretched much more after the treatment with hot water than it could be before. We had no difficulty in making the sample of Saxe measure twenty-four inches and three-quarters, and we have little doubt that a twenty-four-inch print on that paper cut across the roll might, with care in mounting, be made to measure an inch more; so that it will be seen it is quite possible with a portrait on twenty-four-inch paper to make a life-size head a third of an inch larger—that is, if it were on the transverse way of the web.

Our next experiment was with a hand-made paper with long fiber; in fact, one of the round, gray filter papers so well known to most photographers. Each sheet of the larger sizes of these is made separately, and not cut from larger pieces. We took one of these and cut it down to exactly eighteen inches in diameter, and then carefully saturated it with water, placed it on a glass plate as before, and found that it had expanded equally in all directions to the extent of half-an-inch. All the samples were then dried and again measured, and the filter paper was found to contract to its original size exactly; but in all the other samples those cut from the roll transversely were about an eighth of an inch longer than at first.

From these experiments it will be seen that paper cut with the length of the roll practically does not expand at all. This fact should be borne in mind by those who have to produce photographs that have to be joined in the mounting, which is frequently necessary in the case of large copies of maps and charts. When two or more prints have to be joined, and it is found that one is longer than the others, the longest should always be fastened down first. The others may then generally be stretched sufficiently in the mounting to make them match—at least at the junction. Advantage may also be taken of mounting one dry and the others wet, or by using (say) starch for the one, which would cause it to expand, and a solution of gelatine containing a large proportion of alcohol, which has no such property, for the other. With a little judgment, and the adoption of one or other of these dodges, prints of slightly different sizes may be made to match near enough for most purposes.—*Br. Jour. of Photography.*

#### DETECTING FREE HYDROCHLORIC ACID.

By PROF. NICOLA REASE.

THE author finds that a solution of ordinary phenol treated with ferric chloride takes an amethyst coloration, turning to a brown. But if a drop of hydrochloric acid is added to the solution the liquid either assumes no coloration at all or assumes a greenish tint. He proceeds as follows: 1 gm. of the crystalline phenol of commerce is heated in 100 c.c. of pure water. He then pours 1 c.c. of the liquid ferric chloride into 50 c.c. of pure water. This solution being in a small test beaker set on a sheet of white paper, the solution of phenol is added drop by drop. The first drop, if the solution is slightly acid, produces a fugitive coloration, but if it is strongly acid no color appears. On continuing to add the phenol solution the color becomes permanent and gradually darkens. From the volume of the phenol solution consumed an approximate idea of the quantity of acid present may be formed.

#### DECOMPOSITION OF POTASSIUM PERMANGANATE BY OXYGENATED WATER.

By M. BERTHELOT.

THESE two compounds, if brought in contact in a strongly acid liquid, are reciprocally decomposed, losing all their active oxygen, and being reduced to the state of protoxide. This change is due to the formation of an unstable compound, whose spontaneous destruction explains the consecutive evolution of oxygen. This new colorless compound is stable at -12° in the medium where it is produced, but is destroyed on assuming the ordinary temperature. The author regards this compound as a hydrogen tetroxide formed by the oxidation of oxygenated water by potassium permanganate. It is analogous to several peroxides and metallic acids, and to hydrogen tetrathiodide.

#### ON PORTLAND CEMENT.\*

By MR. WATSON.

PRESUMING that the members of this society are not so conversant with the history of the manufacture of Portland cement as with that of soda and its compounds, I will venture to preface this short paper with a biographical sketch of the former, commencing at its birth.

In the year 1824, Mr. Joseph Aspdin, of Leeds, in the county of York, master bricklayer, made application at the Patent Office to protect a process for making cement or artificial stone for stuccoing buildings, water-works, cisterns, or any other purpose to which it may be applicable, and which he called Portland cement. The process of manufacture described in his specification is as follows:

"I take the specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself and cause the puddle or powder, or the limestone, as the case may be, to be calcined.

"I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labor or machinery. After this proceeding, I put the above mixture into a slip pan for evaporation, either by the heat of the sun, or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan till the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln, till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone."

Although Monsieur Vicat, the eminent French chemist, as well as others had succeeded in producing hydraulic cement, closely akin to Aspdin's Portland, long before the date of his specification, and that also by the admixture and burning together of various calcareous and argillaceous substances, there is little doubt that the manufacture of the material known as Portland cement dates from that epoch when Mr. Aspdin filed his specification. How he discovered that the scrapings of the Yorkshire roads could be turned to such good account, there is not evidence to show, but we have proof sufficient that these scrapings when subjected to the manipulation of the observant Yorkshireman, became the pioneer of an important branch of manufacture.

Almost at the same time that Aspdin was experimenting and accomplishing great things with his road mud, Sir C. W. Paisley, of the Royal Engineers, who was stationed at Chatham, was exercising his mind and making elaborate experiments with a view of improving his knowledge of mortars for building purposes, and after sundry trials and failures, he succeeded in making cement identical with Aspdin's Portland, but produced from the chalk and clay of his locality.

Thus, it is curious to observe, Portland cement had its birthplace, although Aspdin had the honor of christening it, in two different places almost simultaneously, and while one inventor secured his raw materials from the hard calcareous and argillaceous formations of the Oolitic system, the other supplied himself from the soft cretaceous chalk strata and the slimy fluviatile accumulations of the post-tertiary period.

Portland cement, like most other young and tender things, was subjected in its early youth to the fierce winds of criticism, and the severe and biting blasts of prejudice, but, as is usually the case when a good thing is offered to the British public, it quickly gained reputation and waxed strong in favor, year by year increasing in demand up to the present, and I think I am under-estimating when, taking last year's statistics as a guide, I calculate the present production in England to exceed half a million tons per annum. The contagion for making Portland cement has likewise spread beyond the shores of the British Isles, a considerable quantity being now made at various places on the Continent where suitable materials are procurable.

Until very recently the process adopted and the machinery employed in the manufacture of Portland cement have varied very little indeed; the *modus operandi* may be described in a few words. The chalk and clay are thoroughly mixed in a pug or wash mill with a large proportion of water amounting to three or four times the weight of the materials. After being well and carefully incorporated, this liquid slurry is pumped or conveyed by other mechanical means to becks or settling ponds, where the heavier portion of the slurry subsides, leaving the superincumbent water necessary for the mixing on the top; this settlement takes many weeks to complete, the water is gradually drawn off, leaving a substance technically called "slip" at the bottom of the beck. This slip is then conveyed by barrows and spread on flats, where it is dried, the requisite heat being derived from coke ovens built beneath the flats. When the moisture is all evaporated, the dried material is removed and loaded into kilns adjoining, fuel being added sufficient for the requisite amount of calcination, the waste heat and gases being liberated through, the chimney or sugar loaf cone of the kiln, which few will have failed to observe who have ever been in the vicinity of a Portland cement manufactory. After the important process of calcination is completed, the clinker is drawn from the kiln, conveyed to the mill, then ground by horizontal millstones and is ready for the consumer.

To those who have been able to follow this rough description it will be apparent that the aim of the cement maker is, in the first place, to secure a thorough and uniform mechanical incorporation of the raw materials he has to deal with; secondly, to preserve or sustain that intimate relationship during the drying process; and, thirdly, to induce perfect and equal chemical combination of the component parts by the application of heat.

It is almost needless to remark that, of course, the primary step is the selection of raw materials suitable for manipulation, and then to decide upon proportions necessary for a successful result, which can only be arrived at by a careful chemical analysis. The object of the cement maker is to produce a mechanical mixture of carbonate of lime and silicate of alumina, the proportions of which are so evenly balanced that only sufficient lime is present to enter into chemical combinations with the silica and alumina in the clay, and produce a double silicate of lime and alumina.

Although the method of manipulation described is still extensively adopted, yet, like all other devices of man, it is crowded with imperfections, and among the multitude of these shortcomings a few may be mentioned. The chalk usually employed does not vary either in chemical proportion

\* A paper read before the Newcastle-upon-Tyne Chemical Society, February 26, 1880.

\* Dr. Wolfram, of Dresden, has patented a process which seems to point in this direction.

† My own experience is that boiling the gelatine is by no means so effectual in increasing the sensitiveness as keeping it hot at a comparatively low temperature for a long period of time. This I attribute to the fact that the products of decomposition of gelatine at a high temperature are different from those produced in a lower temperature.