other permanganates behave in the same way. In fact the permanganates can only be made in the wet way. On the other hand, manganates are generally produced in the dry way, and they will stand a very high temperature.

If, therefore, a substance, after having been heated to the temperature of the blast furnace, would dissolve in pure water with the well known rich purple color of a permanganate solution, it seems almost certain that such a substance could not be a permanganate, but it could be a solution of a ferrate. It is, of course, also possible that the water used to dissolve the substance in question was not pure, but accidentally contained some acid, whereby, on dissolving, the manganate was converted into permanganate.

THE MANUFACTURE OF ACETONE AND OF ACETONE-CHLOROFORM FROM ACETIC ACID.[1]

BY EDWARD R. SQUIBB.

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JUST one year ago, January 11th, 1895, the writer read a paper before this Society upon "Improvement in the Manufacture of Acetone," and this paper was published in the Journal for March, 1895, page 187. The improvement claimed consisted in the use of acetic acid, instead of acetates, and in the use of a rotary still for the decomposition. The results given were obtained from a model apparatus on a table.

During the year that has elapsed since that paper was read, a large rotary still, twelve feet in length by two feet in diameter, has been set up, and this has decomposed in 126 hours about 1,700 pounds of absolute acetic acid, giving about ninety per cent. of the theoretical yield of acetone against about eighty per cent. in the small apparatus.

But the patentees of the processes for making acetone from acetates object to the use of this process and apparatus as being in conflict with their patents.

The acetone produced was converted into chloroform by the Watts (Seimerling) proportions of material in an apparatus described by the writer in 1857,[2] and used for many years in making chloroform from alcohol, and this is also objected to.

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[1] Read before the New York Section, January 10, 1896.

[2] *Ephemeris*, 4, [1], 71.

Under these circumstances it seems necessary to find out what has been done in the past upon this important subject, and what may be the relations of past work to the present conditions, and in this it is hoped the society may be interested.

ACETONE.

It is impossible to determine when or where acetone was first made and used.[1] According to the authority last given, after the time of Boerhaave in 1732, "the body was but little investigated until 1805, when Trommsdorff stated that on distilling acetate of potash or soda, a liquid was obtained which stands between alcohol and ether." In 1807 the Brothers Derosne in Paris[2] studied its properties; and in 1809 Chenevix[3] demonstrated that this substance was obtained by the dry distillation of any one of the acetates.

The correct composition of acetone was first given by Liebig[4] and Dumas.[5]

Further investigations by Kane, 1838, and by Chancel, Williamson, Chiozza, Freund, Wanklyn, and others, still more definitely established the sources, character and properties of acetone, and gave it a definite chemical and economic position so that its production or manufacture by the dry distillation of acetates was as well known as the production of alcohol by distillation from fermented sugars, as early as 1848, when Böttger refers to it as a market article in common use. Wackenroder,[6] in 1848, states that since acetone is quoted on the price lists at ten sgr. (Silbergroschen) per ounce, the preparation of chloroform from it is well worth recommending.

In "Handwörterbuch der reinen und angewandten Chemie herausgegeben von Dr. J. Liebig, Dr. J. C. Poggendorff und Dr. Fr. Wöhler—Redigirt von Dr. Hermann Kolbe, Braunschweig," 1842, Vol. II, p. 1018, is the following (translated) statement:

According to Justus Liebig and Pelouze, the best thing to use

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[1] See Wurtz' Dictionnaire de Chimie, 1873, 1, 31; Gmelin: Handbook of Chemistry, 1855, **9**, 1; Roscoe and Schorlemmer: A Treatise on Chemistry, 1882, **3**, [1], 568.

[2] *Ann. de Chim.*, **63**, 267.

[3] *Ann. der Phys.*, **32**, 191.

[4] *Ann. Pharm.*, 1, 223.

[5] *Ann. Chim. Phys.*, **49**, 208.

[6] *Archiv. der Pharm.*, **53**, 273.

for the preparation of acetone is concentrated acetic acid, which in the state of vapor is conducted through a heated tube of glass, porcelain or iron, which for the sake of increasing surface, is filled with pieces of charcoal, and the products of decomposition are condensed in the usual way. The tube should be heated only to incipient redness; at a higher temperature only empyreumatic oils, combustible gases and charcoal are obtained as the products of the decomposition.

Beside the citations given, the literature on the preparation, properties and reactions of acetone is very copious and definite up to about 1853. After this date the papers published are comparatively few, leading to the inference that the substance had reached a definite position and gone into general use.

In a paper by Prof. Samuel P. Sadtler, Ph.D., "On Recent Improvements in the Methods for the Manufacture of Chloroform," published in *The American Journal of Pharmacy* for July, 1889, p. 321, the following statements are made:

"The old process of manufacture by the action of bleaching powder upon alcohol has given way to what is now termed the 'acetone' process. This is not, however, a new discovery. Liebig, in 1832, in following up his first account of the properties of the newly discovered "chloride of carbon" (chloroform) mentions that it can be gotten in very large quantities by the action of bleaching powder upon 'pyroacetic spirit' (acetone) as well as from alcohol. That alcohol has all this time been preferred to acetone as a material from which to prepare chloroform is due mainly to the fact that only in recent years has acetone been prepared pure in quantity, but also to the erroneous statement of Siemerling, quoted in the works of reference like Watts' Dictionary of Chemistry, that only thirty-three per cent. of chloroform could be gotten from acetone by the action of bleaching powder." . . . "The manufacture of a purer grade of acetone than that then in use for solvent purposes, having been begun in Germany in 1881, on the part of the 'Verein für Chemische Industrie.' Liebig's old suggestion for the manufacture of chloroform from acetone was taken up by the 'Verein Chemischer Fabriken,' Mannheim, Germany, in the beginning of 1882, and a year later by the first mentioned company which made the acetone for both."

From these references it will be seen that the reactions involved in the production of acetone, and the constitution, character, properties and reactions of acetone had been long and well known prior to 1848, and that it had been made and utilized on a large scale prior to 1882 ; and further, that it had been produced both by the dry distillation of acetates, and by the wet distillation of acetic acid, as a matter of open knowledge and practice.

This condition of the scientific knowledge of an important chemical substance throughout France and Germany—and throughout the scientific world—makes it very certain that the chemical industries, which depend upon such knowledge for their origin and progress in general, but do not publish their processes—availed themselves of this knowledge and of this chemical agent.

In June, 1886, application was filed in the U. S. Patent Office, and two years later, in July, 1888, Letters Patent No. 385,777 were issued to Gustav Rumpf for the invention of a "new and useful Improvement in the Manufacture of Acetone," and from the specifications and claims of this patent the following extracts are made :

"In making acetone by dry distillation of acetates, as acetate of lime, it has, before my invention, been thought possible to obtain only less than half the acetone."

"Dr. Herman Hager, in his Handbuch der Pharmaceutischen Praxis, published in Berlin in 1882, states under the head of 'Acetone,' 'that it is possible to obtain an average yield from chemically pure acetate of lime of only fifteen per cent. of acetone, while the theoretical yield from chemically pure acetate of lime is thirty-four per cent.' "

"I have discovered that if the acetates are subjected for distillation to a low heat and approximately uniform temperature and the process extended over several hours, the yield of acetone will be greatly increased, and will approach very nearly the theoretical yield of any particular acetate, which in the case of good gray or commercial acetate of lime is about twenty-seven per cent. I have also discovered that in the process of subjecting acetates in a closed vessel to heat applied externally to the vessel for distilling acetone from the acetates the desired slowness of distillation and uniformity of temperature may be secured by stirring the acetates so that all portions of the mass will be subjected to the heat resulting from direct contact with the bottom of the vessel, and by admitting free steam from time to time into direct contact with the acetates in case of any undesirable rise in temperature within the vessel.''

''My invention consists in an improvement in the method of obtaining acetone from acetates by destructive distillation, consisting in subjecting the acetates in a closed vessels to slow destructive distillation at a low and approximately uniform temperature, and it is also well to stir the acetates during such distillation.''

The claims are to—

''The improvement in the method of obtaining acetone from an acetate consisting in subjecting the acetate in a closed vessel to slow destructive distillation at a low and approximately uniform temperature.''

This first broad claim is based, not upon the chemical reaction which was well known, nor upon the destructive distillation by heat, which was a well known process, but upon an improvement in the apparatus and management by which the yield of acetone was alleged to have been increased. But the evidence upon which the increase is claimed is an erroneous statement quoted from Hager—erroneous because it is hardly practicable through any ordinary degree of want of knowledge and skill to obtain so little as fifteen per cent. of acetone from acetate of lime.

The second claim is to a stirrer in its effects on the process. But a stirrer is a device so common in chemical processes that no such application of it can be considered original or new.

The third claim to the effect of the introduction of steam during the distillation is much better.

The fifth, sixth, seventh and eighth claims are to improvement in the process of purifying the crude acetone by means of lime, dilution and rectification, and these are but the steps common to all such operations.

It is upon this patent that infringement is charged, when it is simply putting into use the very old process of making acetone by the destructive distillation of acetic acid in a rotary still as described in a paper on "Improvement in the Manufacture of Acetone," read before this New York Section of the American Chemical Society on January 11, 1895, and published in the Journal for March, 1895, p. 187, and in *An Ephemeris of Materia Medica, Pharmacy, Therapeutics and Collateral Information*, Vol. IV, No. 3, p. 1653.

The writer makes acetone by the destructive distillation of the watery vapor of acetic acid in a rotary still, in the presence of barium carbonate or pumice-stone or bone-charcoal, barium carbonate being preferred, because being a very heavy powder, a larger charge of smaller volume can be used.

The patentees claim only acetates as their material, but claim infringement by the use of acetic acid, because acetic acid is made from acetates, and acetates are made from acetic acid; and secondly, claim infringement on the ground that acetate of barium is first formed, and then decomposed in the rotary still, and therefore the process is really not a destructive distillation of acetic acid, but of barium acetate—one of the class of acetates claimed as secured to them by their patent, although in use for this purpose for so many years. That is, it is claimed that an acetate of barium is formed under conditions of temperature in which an acetate of barium cannot exist. Barium acetate decomposes at about 400° to 405° C. by an ordinary pyrometer. Acetic acid is best decomposed at about 500° to 525° C. by the same pyrometer, and yet it is claimed that at 500° C. barium acetate forms momentarily and then is instantly decomposed. That is, it is formed in an atmosphere in which it cannot exist for an instant, and in which acetic acid cannot exist.[1]

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[1] Upon this point the patentees were very decided in the statement, based not only on their own experience, but also on the experience of their German correspondents, that if the barium carbonate was replaced by pumice-stone the amount of acetone obtained would be too small to have any commercial importance. This result had been confirmed to them by so many trials that at their suggestion, and in order to satisfy them that their results were not trustworthy, the following experiments were made after the above paper was written, but before it was published.

The large rotary still was emptied and cleaned out by sweeping, scrap-

But, quite apart from this, the chemical reaction by which acetone is produced, whether from acetates or from acetic acid, was well known for more than half a century before the date of this patent. What is really covered by the patent is certain specified and described apparatus and management whereby an improved yield is to be obtained from acetates, and from acetates only, for the apparatus and management are not at all applicable to the use of acetic acid, and are not used either in form or substance.

ACETONE-CHLOROFORM.

The history of acetone-chloroform dates distinctly back to 1832. In the *Annalen der Pharmacie, 1832*, **21,** 198, Liebig describes the preparation of chloroform in large quantity, from given proportions of hypochlorite of lime, water, and alcohol, and he says the yield will be equal in weight to the alcohol used. He then goes on to say that chloroform may also be obtained in large quantity by treating acetone with hypochlorite of lime under the same conditions.

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ing, and finally by sponging with water until it was quite free from any appreciable quantity of barium salt. It was then closed and run empty with a continuous feed of acetic acid for periods of three hours each, at the following temperatures, the rate of feeding, and the assaying for acid and acetone being approximate only, and only trustworthy by averaging.

At 300° C. 22.3 pounds of absolute acid was run in and
19.5 " " " " " received without any acetone or any evidence of decomposition of the acid, the 2.8 pounds of acid not accounted for being the normal charge of the apparatus.

At 350° C. 38.3 pounds of absolute acid was run in and
38.1 " " " " came through with no signs of any decomposition,—no acetone.

At 400° C. 36.1 pounds of absolute acid was run in and
29.9 " " " " " received undecomposed, leaving
6.2 " " " " decomposed, and this decomposed acid gave 97 per cent. of the acetone required by theory.

At 450° C. 35.1 pounds of absolute acid was run in and
18.5 " " " " " received undecomposed, leaving
16.6 " " " " decomposed, which apparently gave 112 per cent. of the acetone required by theory.

At 500° C. 41.4 pounds of absolute acid was fed in and
10.8 " " " " " received undecomposed, leaving
30.6 " " " " decomposed, which apparently gave 104 per cent. of the acetone required by theory.

At 5.50 C. 40.4 pounds of absolute acid was fed in and
5.1 " " " " " received undecomposed, leaving
35.3 " " " " decomposed, which apparently gave 82 per cent. of the acetone required by theory.

Liebig does not give the yield from acetone, but after giving the yield from alcohol as being equal in weight to the alcohol used, he says it is obtained in large quantity from acetone.

In 1835 Dumas and Peligot[1] state that when a solution of hypochlorite of lime is distilled with wood spirit there is obtained, as a matter of fact, some ordinary chloroform. The experiment is as easy as with alcohol or acetone.

Then a run of twenty-four hours was made at the last temperature, 550° C. to give opportunity for closer determinations of results.

321 pounds of absolute acid was fed in and
57.3 " " " " " received undecomposed, leaving
263.7 " " " " decomposed, which apparently
gave 97 per cent. of the acetone required by theory.

The still was then opened, charged with 130 pounds of coarsely ground pumice-stone, and a parallel series of experiments made.

At 300° C. 41.8 pounds of absolute acid was fed in and
39.1 " " " " " received undecomposed, leaving
2.7 " " " " decomposed, which apparently gave 33.5 per cent. of the acetone required by theory.
At 350° C. 39.6 pounds of absolute acid was fed in and
34.8 " " " " " received undecomposed, leaving
4.8 " " " " decomposed, which apparently gave 87.5 per cent. of the acetone required by theory.
At 400° C. 41.8 pounds of absolute acid was fed in and
28.5 " " " " " received undecomposed, leaving
13.3 " " " " decomposed, which apparently gave 97 per cent. of the acetone required by theory.
At 450° C. 41.8 pounds of absolute acid was fed in and
13.0 " " " " " received undecomposed, leaving
28.8 " " " " decomposed, which apparently gave 95 per cent. of the acetone required by theory.
At 500° C. 43.4 pounds of absolute acid was fed in and
8.8 " " " " " received undecomposed, leaving
34.6 " " " " decomposed, which apparently gave 96.4 per cent. of the acetone required by theory.
At 550° C. 43.4 pounds of absolute acid was fed in and
7.4 " " " " " received undecomposed, leaving
36.0 " " " " decomposed, which apparently gave 100 per cent. of the acetone required by theory.

Then a run of twenty-four hours was made at the last temperature, 550° C., as a check upon the previous results.

345.5 pounds of absolute acid was fed in and
69.5 " " " " " received undecomposed, leaving
276.0 " " " " decomposed, which apparently gave 104 per cent. of the acetone required by theory.

This last, and three other impossible results are as yet unexplainable, but they may be reasonably charged to the uncertainties in the use of an hydrometer and the iodoform process of assaying.

[1] *Ann. Chim. Phys.*, **58**, 15.

Liebig in his text-book[1] gives a formula and directions for the manufacture of chloroform from either acetone, alcohol, or wood spirit, and gives to acetone the leading place.

M. Bonnet[2], at a meeting of the Academy, says, "I have obtained in the distillation of equal parts of acetate of lime and hypochlorite of lime, in a stone retort, a very large quantity of chloroform, and far more easily than by the methods of preparation that are known.

Dr. Reich[3] proposed and used hypochlorite of sodium in place of hypochlorite of lime on account of the uneven amount of chlorine in the latter. He distilled together two pounds each of hypochlorite and acetate of sodium and received five to six drams of chloroform and twelve to fourteen ounces of acetone and water. This latter was again distilled with four to six ounces of hypochlorite, and again a considerable amount of chloroform and acetone was received. The last operation was repeated with a new portion of hypochlorite, and then the total amount of chloroform was eight to ten ounces, with still some excess of acetone for future operations.

Acetone when distilled with sodium hypochlorite yields chloroform in the proportion of four ounces of acetone to five to five and one-half ounces of chloroform.

Prof. Böttger[4] distilled together equal quantities of commercial bleaching powder and crystallized sodium acetate and obtained chloroform and acetone. Then he distilled the excess of acetone with a fresh portion of bleaching powder and had "great joy in seeing from this second operation a very considerable quantity of the purest chloroform distil over together with some acetone still undecomposed." The excess of acetone was again distilled with fresh bleaching powder and the process repeated until by three to four distillations all the acetone was used. The yield of chloroform being about four ounces to each pound of bleaching powder.

Chloroform made directly from acetone, which he says is at present, 1848, to be had in the market, is obtained in the propor-

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[1] Traité de Chimie Organiques, I, 576.

[2] L'Institut. No. 196 Februar. 1837.

[3] *Archiv. der. Pharmacie*, Zweite Reihe, *1848*, 55. 65.

[4] Polytechnisches Notizblatt. *1848*. 3. 1.

tion of one ounce and two drams of chloroform from one ounce of acetone.

Still in the year 1848 Prof. Heinrich Wackenroder,[1] one of the editors of the *Archiv*, says in substance: "The great practical interest in chloroform at the present time calls, first of all, for a closer examination of the methods for making it. Therefore I have induced Mr. Siemerling to undertake, in my laboratory, some experiments relating to the preparation of chloroform which are in the most recent publications on the subject. Although these experiments have in no respect given the results which were hoped for, it nevertheless seems to be worth while to call attention to them for the sake of the future continuation of the subject."

Then follows the paper of Mr. V. Siemerling, and at page 26: "II. Preparation of Chloroform from Acetone."

"According to the statement of Prof. Böttger, one ounce of acetone, which has been mixed with hypochlorite of lime to a pasty mass, should give one ounce and two drams of chloroform. As this seemed to be an easy and advantageous method of preparation, some experiments were made with acetone procured from the factory of Trommsdorff, in Erfurt, but they did not accord with the statement of Böttger."

"In the first experiment (*a*) thirty grams of acetone were mixed with fifty grams of hypochlorite of lime and fifty grams of water and distilled. The chloroform was separated and rectified with concentrated sulphuric acid. The yellow chloroform thus obtained was again rectified from burnt lime when it had an empyreumatic odor—quantity not given."

In experiment (*b*) thirty gram of acetone, 120 of hypochlorite and enough water to make a pasty mass, were mixed and distilled. It is true much chloroform came over, but there was also undecomposed acetone as well. It was repeatedly washed with water and rectified over calcium chloride, in which rectification there was a pretty large loss every time, but the number of times is not given. The yield was nine grams.

Experiment (*c*), since in both experiments undecomposed acetone distilled over the quantity (proportion) of hypochlorite was

[1] *Archiv. der Pharmacie*, *1848*, 54, 23.

increased, and thirty grams of acetone to 150 grams of hypochlorite, with water, were mixed to a pasty mass, allowed to stand twenty-four hours, and were then distilled. The product contained much chloroform, but also undecomposed acetone; therefore it was put back into the retort with forty grams of fresh hypochlorite and again distilled. The chloroform thus obtained still contained acetone, from which it was purified by repeated washing with water, and then rectified over calcium chloride. The yield was ten grams of chloroform.

Another experiment (*d*) is given wherein twenty grams of acetone and sixty grams of hypochlorite were distilled together without water, but with unfavorable result, the yield being six grams of chloroform.

The specific gravity of the chloroform obtained from acetone, after repeated rectifications over calcium chloride was only 1.31, and it always contained some acetone; and the largest yield by Böttger's process was one-third of the acetone used. This differs considerably from his statement that one part of acetone yielded one and one-fourth parts of chloroform.

Siemerling than goes on to say, that if we assume with Liebig, that acetone is composed of one atom of acetyl oxide and one atom of methyl oxide, and explain in this way the formation of chloroform, from methyl oxide it naturally follows that we must get less chloroform than the acetone used.

The sum of the elements of one atom of acetyl oxide $=C_4H_6O$ and one atom of methyl oxide $=C_2H_6O$ is equivalent to two atoms of acetone $= C_6H_{12}O_2$. In thirty grams of acetone there are therefore 11.8 grams of methyl oxide, which, since four atoms of methyl oxide consist of the same elements as two atoms of alcohol, can form 15.1 grams of chloroform, assuming that complete decomposition takes place.

According to the theory, half of the acetone used must be recovered as chloroform; but since in the practical manufacture of chemical products the quantity prescribed by theory is never obtained, it should be considered a favorable result when one-third of the acetone used is obtained as chloroform, especially as the experiments were made only on the small scale.

From these experiments, it follows that the preparation of chloroform from acetone is quite unfit for practical use. Were even the quantity of chloroform stated by Böttger as obtainable from acetone possible, it would have the disadvantage of being freed from acetone with very great difficulty.

The paper of Siemerling, from which the above abstract is made, seems to have received the endorsement of Wackenroder, although it controverts the statements of both Reich and Böttger, and it may be from his high authority as much as from the paper itself that the results seem to have been accepted and quoted by Gmelin,[1] Watts,[2] and other reference authorities, and the influence of the publication seems to have been, so far as the literature of the subject goes, to prevent or obstruct the acetone process for many years. As it was so long and so well-known, manufacturers may have been, and probably were using the process privately, but up to 1881–1883[3] very little information on the subject is found. Still the work and the conclusions of Siemerling must have been known to be grossly erroneous by every one whose interest it became to try them. Calculations would show to anyone that when ordinary acetone and bleaching powder were used the proportions required are about one to ten, or about double the largest proportion of hypochlorite used by Siemerling, and the resulting chloroform should be about double the weight of the acetone used; and many who preceded Siemerling knew better than he how to save and utilize the great excess of acetone, or deficiency of hypochlorite taken.

But the Siemerling results were very faulty and very misleading in other respects. The present writer having learned from all the work of the past on the subject, that any excess of acetone used could be easily recovered and used again, added to this knowledge from his own experience the fact, that, where an excess of acetone was taken, the hypochlorite was more economically and more promptly utilized, and the resulting chloroform was cleaner. Having gained from the Siemerling process this step the writer was prepared to try that proportion and process critically, and he found that, as a table experiment, it was

[1] Handbook of Chemistry, Vol. VII, 346.

[2] Dictionary of Chemistry, *1883*, 1, 918.

[3] Sadtler, *Am. J. Pharm., July*, *1889*, 321.

quite impracticable by any reasonable degree of mismanagement to obtain so low a result. In two fairly careless trials from thirty grams of ninety-six per cent. acetone the yield of chloroform was twenty-three grams in one case and thirty-two grams in the other, instead of Siemerling's ten grams. In larger trials of his proportions up to 280 pounds of absolute acetone to one cask of 1400 pounds of thirty-three per cent. bleaching powder in one charge the yield was not less than 200 pounds of chloroform, and about 130 pounds of recovered acetone, thus proving conclusively the gravity of the unaccountable errors of the Siemerling work, and showing a basis for the mischief done by this bad work.

Looking back from this later day at the authoritative way in which these mistakes and misstatements of Siemerling were published and quoted, it is easy to see that nothing could be better adapted to obstruct or prevent any increase in the general production of acetone-chloroform, and to confine its productions to those manufacturers who were using the process secretly.

One of the definite evil consequences of this Siemerling paper was the adoption of its erroneous results as the basis of the following patent.

On June 23, 1886, Gustav Rumpf applied for a patent, and on July 5th, 1888, patent No. 383,992 was issued to him for the invention of "A New and Useful Improvement in the Manufacture of Chloroform from Acetone," of which the following is a specification: "The essential feature of this invention is based on the discovery that acetone when treated in the proper way with a hypochlorite—for example chloride of lime—will yield a larger quantity of chloroform than has been heretofore known. Watts, in his Dictionary of Chemistry, edition of 1883, **1**, 918, says that the manufacture of chloroform from acetone cannot usefully be carried out, not only because the price of acetone is too high, but particularly because acetone yields about thirty-three per cent. of its own weight of chloroform when it is treated with chloride of lime. Watts distilled thirty grams of acetone with 150 grams of chloride of lime, and rectified the watery distillate with forty grams of chloride of lime. I have discovered a method whereby it is possible to obtain a yield of chloroform from acetone very much greater than that obtained by Watts. I have found that the reaction may be made to take place in such a way that one equivalent of acetone will yield one equivalent of chloroform by volume, or about 180 per cent. by weight, and the advantages of my invention may be secured in a greater or less degree by properly employing with about fifty-eight pounds of acetone more than 300 pounds of good chloride of lime. The best results and greatest yield of chloroform can, as I have found, be obtained by the use of, say, fifty-eight pounds of acetone to at least 600 pounds of a good chloride of lime containing about thirty-five per cent. of available chlorine, and in proportion if the chloride of lime is poorer. The yield of chloroform will then be from 150 per cent. to 180 per cent. of the weight of the acetone employed instead of about thirty-three per cent.

Then follow claims for invention of diluting the acetone and of introducing it periodically during the process—of introducing it below the surface of the solution in the still—of the use of a mechanical stirrer, and of the use of a still and condenser which are described and figured.

The basis upon which this patent rests, for its reason to be, is the quotation from Watts' Dictionary. Watts quotes the process from *Gmelin's Handbook*, and Gmelin quotes it from *Siemerling's Paper* in the *Archiv der Pharmacie*, *1848*, **54**, 26. Now, as the paper and quotations are grossly erroneous, and as writers of preceding papers publish results that approximate those of the patent, it might reasonably be asked what is the value of the patent. But the present writer, while intending to make acetone-chloroform, very earnestly desires to avoid all question in regard to the validity of this patent, and therefore uses the Watts (Siemerling) process, which is outside the limit claimed by the patent, with an entirely different apparatus and management described by him in 1857, and republished in *Ephemeris*, **4**, [1] 71.

It is proposed to use charges of 280 pounds of absolute acetone to 1,400 pounds of thirty-five per cent. bleaching powder, one to five—to pass the resulting chloroform through scrubbers, then distil it through water, then distil it from a small portion of bleaching powder, then pass it through sulphuric acid scrubbers, and finally rectify it in three fractions, the large middle fraction being accepted, and the others being worked over.

A part of the great excess of acetone taken in the one to five proportion is recovered by continuing the distillation after the chloroform is all over. Another part is recovered in the wash water from the scrubbers and the distillation, and the small remainder is decomposed by the small proportion of bleaching powder, the total amount recovered being practically not far from the total excess.

To this recovered acetone, carefully assayed, new acetone is added to make up the 280 pounds for the next charge.

The patentees were invited to see this apparatus and process in order to convince them that there is a strong desire to avoid any color of infringement by taking the Siemerling proportions which are excluded from their patent. But they took the ground that this was a mere evasion, or getting round their patent by using the excess of acetone over again, and could not be made to see that this, if objectionable, is so by defect in the equity of the patent, and is a proceeding that ante-dated the patent by many years. And finally they covered everything by claiming that the patent secured to them the sole right to make chloroform from acetone in the United States, thus claiming a reaction that had been well known for more than fifty years.

As to the reasons why large manufacturers of chloroform did not avail themselves earlier of the acetone process, the first answer is that it is probable that many of them, in Germany, at least, did so secretly as soon as acetone became cheaper than alcohol.

But, as to other more positive reasons, the writer, as having been for many years a large manufacturer from alcohol, and as having, with all other makers, given up the manufacture rather than contest this patent, can only speak for himself. He for many years doubted the identity of alcohol and acetone-chloroform, and doubted whether the latter was as easily purified for use as the former, so that when chloroform was offered to him at so low a price as to insure that it was made from acetone it was refused. Chloroform has always been a most important agent, and during the earlier part of its career the numerous fatalities from its use were charged to its impurities, so that the alcohol process was adhered to until the identity of the products from alcohol and acetone was fully proved,—not only chemically, but also by surgical experience of considerable duration. Then as time passed and the subject came up for research and reconsideration, the Siemerling results came up also and settled the question against acetone.

Finally Dr. Gustav Rumpf, a German, and an employé for some years in an acetone-chloroform manufactory in Germany, where there is no patent, came to this country, took out these patents and assigned them to the present holders, so that now for the past seven years or more any one making acetone-chloroform in this country by processes that had been free and largely used in Germany for many years, was liable to prosecution for infringement.

Having any general knowledge of the history of acetone and acetone-chloroform, it is difficult to understand how such patents could be issued that would claim to control the proportions of well known chemical materials in long known chemical reactions. But such patents were issued, and, therefore, command respect. That the processes were not used earlier in this country may be charged chiefly to the endorsements of the Siemerling paper; and that the patents appear to have been so long acquisced in is due to the circumstance that any one who might contest them would do so at great cost of money, time and annoyance in defensive litigation, which, if successful, would secure the benefits equally to many manufacturers, and to the public in lower prices of the products, whilst the contestant would bear all the costs.

In seeking new outlets for acetic acid the writer determined to convert the acid into chloroform, and determined also to respect these patents. In the intermediate step of making acetone, acetic acid was used, not to evade the patents, but because by its use the impurities of the crude acetates of lime were avoided, and a larger yield of better acetone was obtained. In the use of acetic acid instead of the acetates of the patent an entirely different apparatus and management are required and used, and if the patent did not exist the writer would not use either its apparatus or management, but would prefer the rotary still and the continuous process.

With regard to the other step wherein the acetone is converted into chforoform, this is accomplished by a reaction that was long and well known before the date of the patent, and the proper portions of the material required for the reaction were easily obtainable by calculation, and this knowledge also ante-dated the patent. The patent then simply covers a specially devised and described apparatus and management which the writer does not use and does not want to use even if they were not patented, but much prefers his old form of apparatus and management described in 1857, and used for many years in making alcohol chloroform. And the successful use of this apparatus and management for acetone chloroform is simply in accordance with the statement of Liebig, in 1832, that acetone could be successfully used under the same conditions as alcohol.

PYRIDINE ALKYL HYDROXIDES.[1]

BY A. B. PRESCOTT AND S. H. BAER.

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THE HYDROXIDES OF QUATERNARY NITROGEN BASES IN GENERAL.

TETRAMETHYL and tetraethyl ammonium hydroxides were well described by their discoverer, A.W. Hofmann,[2] in 1851. Their crystallization in a vacuum, their behavior as alkalies in reaction with the metallic salts, and their conversion to carbonates upon exposure to the air were then set forth. Various quaterary bases of mixed formation from methyl, ethyl, amyl and phenyl were made by Hofmann at the same time. The tetrapropyl ammonium hydroxide was first described by Roemer, in 1873.[3]

The decomposition of quaternary ammonium hydroxides by heat was reported upon by A. W. Hoffmann, in 1881,[4] also by Lawson and Collie, in 1888.[5]

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[1] Read at the Cleveland meeting.

[2] Phil. Trans., *1851*, (2), 357; *Ann. Chem.* (Liebig), **81**, 253, **86**, 292, **91**, 33.

[3] H. Roemer, *Ber. d. chem. Ges.*, **6**, 786.

[4] *Ber. d. chem. Ges.*, **14**, 494.

[5] *J. Chem. Soc.*, **53**, 634.