DEPARTMENT OF THE INTERIOR
UNITED STATES GEOLOGICAL SURVEY
GEORGE OTIS SMITH, DIRECTOR

WATER-SUPPLY PAPER 226

# THE POLLUTION OF STREAMS BY SULPHITE PULP WASTE

## A STUDY OF POSSIBLE REMEDIES

BY

EARLE BERNARD PHELPS

Investigation made at the Sanitary Research Laboratory and Sewage Experiment Station
of the Massachusetts Institute of Technology

WASHINGTON
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# ILLUSTRATION.

# THE POLLUTION OF STREAMS BY SULPHITE PULP WASTE—A STUDY OF POSSIBLE REMEDIES.[a]

By Earle Bernard Phelps.

## INTRODUCTION.

The pollution of streams by the waste liquors resulting from the manufacture of paper pulp by the sulphite process constitutes one of the most serious stream-pollution problems with which science has to deal at the present time. The seriousness of the problem is the direct result of two factors—the tremendous volume of such waste liquors and their high content of organic matter of extremely undesirable character. An approximate estimate of the amount of sulphite waste liquor discharged into the streams of the United States in one year is given in the subjoined statement, compiled from data in Forest Circular No. 120, Forest Service, United States Department of Agriculture.

*Amount of sulphite waste liquor discharged into streams of the United States during 1906.*

| | Million gallons. |
|---|---|
| Maine | 560 |
| Massachusetts | 45 |
| Michigan | 175 |
| New Hampshire | 380 |
| New York | 1,000 |
| Ohio | 41 |
| Oregon | 52 |
| Pennsylvania | 217 |
| Virginia | 84 |
| West Virginia | 89 |
| Wisconsin | 540 |
| All other States | 44 |
| | 3,227 |

According to the above estimate, the total amount of this liquor discharged into streams throughout the country in one year is more than three billion gallons, and when it is considered that of this enormous amount 10 per cent by weight, or more than 2.5 billion pounds, is solid matter, mostly organic, it will be readily conceded that the problem of its disposal is one of no small magnitude.

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[a] This investigation was made in cooperation with the sanitary research laboratory and sewage experiment station of the Massachusetts Institute of Technology.

## STREAM POLLUTION BY SULPHITE PULP WASTE LIQUOR.

### GENERAL DISCUSSION.

Though the pollution of streams by sulphite pulp waste is an obvious and serious matter in the region where sulphite mills exist, the literature contains but few references which throw any light on the actual damage caused. In Germany the regulations of the sanitary authorities are strict. Ahrens [a] states that pulp manufacturers, in spite of constant endeavor, may come into conflict with the authorities because they are not able to meet the requirements in regard to the discharge of waste waters into rivers, and he adds that many factories in Germany have actually been obliged to shut down for that reason. Sanitary officers in the United States are more lenient. This is due partly to the fact that the streams in this country are larger and the greater number of the sulphite mills are located in less densely populated regions.

### POLLUTION OF LAKE CHAMPLAIN.

In some places stream pollution from this cause has been so serious as to warrant investigation. Leighton,[b] in his investigation of the pollution of Lake Champlain, made a study of sulphite pulp waste as it affects Ausable River, which he found to be a black, foul, grossly polluted stream in which the existence of fish or other forms of life is impossible. He concluded, however, that the great dilution of the river waters by those of the lake renders the pollution insignificant so far as the lake waters are concerned.

### POLLUTION OF JAMES RIVER.

Levy[c] made a careful study of the effect of sulphite waste pollution on James River. The sources of pollution are at Covington, Va., about 250 miles by water above Richmond, whose public supply is derived from this stream. Levy found Jackson River, into which this liquor is discharged and which unites with the Cowpasture below Iron Gate to form the James, to be perfectly clear and colorless. The waste entering the stream first turns the water dark brown and later a purplish black. Foam is created at the outfall and wherever the stream is interrupted by falls or by rapids. This appearance can be noted for the entire distance from Covington to Richmond. Dilution is practically the only means of improvement. On the sanitary side of the question Levy considers two problems—(1) whether

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[a] Zeitschr. angew. Chemie, 1895, p. 41.

[b] Leighton, M. O., Preliminary report on the pollution of Lake Champlain: Water-Supply Paper U. S. Geol. Survey No. 121, 1905.

[c] Levy, E. C., Report to the water committee on the investigation of the effect of trades wastes on the water of James River at Richmond. Richmond, 1905.

the substances introduced are themselves actually injurious to health, and (2) what influences they may have on the multiplication of bacteria. The liquor itself as it enters the river is absolutely sterile, not only on account of the actual germicidal substances which it contains, but also on account of the fact that it has been subjected for about twelve hours to steam under a pressure of 80 pounds to the square inch. Its germicidal properties are shown in the following table:

*Germicidal action of sulphite waste liquor on bacteria in highly polluted water from Shockoe Creek.*

[By E. C. Levy.]

| Per cent, by volume, of liquor in mixture. | Number of bacteria per cubic centimeter. | | | Per cent of reduction (−) or increase (+). | |
|---|---|---|---|---|---|
| | At start. | After 6 hours. | After 24 hours. | In 6 hours. | In 24 hours. |
| 0 (control) | 450,000 | 900,000 | 2,500,000 | +100 | + 455 |
| 1 | 445,000 | | [a] 7,500,000 | | +1,585 |
| 5 | 427,500 | 60,000 | 170,000 | − 86 | − 60.2 |
| 10 | 405,000 | 35,000 | 0 | − 91.4 | − 100 |
| 25 | 337,500 | 10 | 0 | −100 | − 100 |

[a] Plate liquefied.

The number of bacteria in the water at the commencement of the experiment is calculated from the number of bacteria present in the creek water itself (450,000). Where the reduction is more than 99.95 per cent it is given as 100 per cent. Even very small amounts of the waste liquor have an antiseptic action, but are not actually germicidal; they restrain the growth of bacteria without killing them. Such action may be harmful rather than otherwise, for in a stream receiving sewage certain kinds of bacteria eventually render the sewage harmless. It would seem that as the character of this waste is so stable it does not furnish food for bacterial growth.

Complaint is made that the water of the James at Richmond is unfit for boiler use, both on account of its corrosive action and on account of the "priming" due to vegetable matter present. Aside from the matter of actual harm, however, Levy states that the water is rendered objectionable in appearance by this waste. The dark-brown, almost black water, with its accumulation of dirty scum, is not relished by the consumer, even if he knows that it is probably safe to drink it. In a bath tub this color is very pronounced, and even in so small a quantity as a tumblerful it is decidedly noticeable. James River is practically clear for certain periods of each year, and at such periods, under normal conditions, no further treatment than mere storage would be required for furnishing satisfactory water. But during these periods, on account of the low stage of the river, the trouble from Covington is most marked. Plain sedimentation has absolutely no effect on the color; but coagulation will remove a large part of it, and Levy found not less than 3 grains of alum per gallon necessary for this purpose. He estimates that with a daily consumption of 14,000,000 gallons it would cost $75 a day for alum, which would not be required if it were not for the sulphite pollution, and states that even then the water would not be perfectly satisfactory.

Farther up the river complaints have been made that fish have been killed by the sulphite waste. The opinion is expressed that if fish are killed it is perhaps because the free oxygen, which is necessary for their life, is used up, rather than because of the presence of substances actually poisonous in themselves.

## POLLUTION OF POTOMAC RIVER.

Some experiments to determine the effect of sulphite waste pollution on fish life in Potomac River are reported by Marsh.[a] He found a decidedly injurious effect on fish of different kinds in dilutions varying in strength from 1 part of waste liquor in 50 parts of water to 1 part in 200 parts of water.

## POLLUTION OF BLACK RIVER.

Whipple[b] has referred to the effect of sulphite pollution on the water supply of Watertown. He states that the sulphite liquors contribute to the odor and color of the water, and necessitate the use of greater amounts of alum than would otherwise be necessary.

## MANUFACTURE OF SULPHITE PULP.

In order that the character and amount of the waste liquors resulting from the manufacture of wood pulp by the sulphite process may be comprehended it will be necessary to describe, in some detail, the various operations that are conducted in a sulphite mill to convert spruce logs into paper pulp. The processes in use at the Mechanicsville mill of the West Virginia Pulp and Paper Company will be described, as they are typical of a modern sulphite mill of average capacity. Though there are naturally many variations in minor details, the essential steps are similar at all mills, so that a detailed description of the processes of one mill, with an occasional statement of important alternative methods, will serve the purpose of this discussion.

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[a] Marsh, M. C., in Parker, H. N., and others, The Potomac River basin: Water-Supply Paper U. S. Geol. Survey No. 192, 1907.

[b] Whipple, G. C., Proc. Watertown Soc. Eng., Watertown, N. Y., 1906.

## THE WOOD.

Spruce and hemlock are the woods used almost exclusively for the manufacture of pulp by the sulphite process. The logs are either barked by hand in the woods before seasoning or by machinery at the mill. Machine barking necessitates cutting the log into 2-foot lengths; in hand work 4-foot lengths are used without further cutting. Machine barking also causes some waste of material through cutting too deeply into the log. Some measurements of logs barked by machinery show that the original circular section of the log had been changed to that of a circle minus 6 small segments, the area of the segments being found to be 18 per cent of that of the original circle. All logs are carefully inspected at the mill, and those in which there is evidence of decayed portions or unremoved bark are rejected. Subsequently a man removes the bark and decayed places from these imperfect logs with an ax. The logs are thrown into a large tank of hot water to loosen the ice, dirt, and sand which have adhered to them. They then pass through scrubbers, in which a powerful spray of water removes all the sand and cinders. They are then ready for the chipper. This machine consists essentially of three knife blades in a rapidly revolving vertical steel disk. One end of the log is pressed against these blades at an angle, and in a few seconds the log is reduced to chips. The resulting fragments are then run over screens to separate them into three portions. Everything that passes through a ¼-inch mesh is discarded. This chip dust is at present practically a waste product, though it is used to some extent for packing ice and for bedding horses. A half-day test at the Mechanicsville mill showed that 1,375 pounds of chip dust, or about 2.7 per cent of waste, resulted from chipping 17 cords of wood. The chips which do not pass through a 1-inch mesh are next separated and passed through a machine known as a shredder. This machine, working on a novel principle, crushes the large chips into shreds and separates the good wood from the knots to a large extent. The shredded mixture is then "floated" over a long water tank, in which the knots, by virtue of their greater specific gravity, sink to the bottom. The separation here is almost complete, and the removal of the knots at this time is of great benefit, as they interfere seriously with subsequent operations. The middle portion of the chipped mixture, which is retained on a ¼-inch screen and passes through a 1-inch screen, goes directly by belt conveyors to the storage bins over the digesters, as does also the floated portion of the shredded chips after a second screening. The chips are now ready for the digester.

## THE ACID LIQUOR.

The solution of chemical reagents used in the digester to dissolve out of the wood all intercellular and other noncellulose matter consists essentially of calcium and magnesium bisulphites with an excess of free sulphurous acid. It is made by passing sulphur dioxide through a suspension of milk of lime made from dolomitic lime, or through towers of limestone over which water is trickling. The former process is in most general use in this country. A suspension of slaked lime (milk of lime) is made, having a strength of about 1.2° B.—that is, about 1.3 per cent $Ca(OH)_2$. Gaseous sulphur dioxide is prepared either by roasting pyrite or by burning sulphur directly in specially designed burners. The gases are passed through lead pipes submerged in large tanks, through which cold water is running, as it is essential to keep the absorption apparatus as cool as possible. The cooled gas next goes into a tank of milk of lime, which is nearly saturated by allowing the gas to enter at the bottom and to bubble up through the liquid. The unabsorbed gas is conducted from the top of this tank to the bottom of a second tank filled with fresh milk of lime, where the absorption is completed. The residual gases then pass to the pumps, which maintain a partial vacuum in the tanks and insure a constant flow of gas. During absorption the contents of the tank are constantly stirred. When the acid liquor in the first tank is of the requisite strength, as shown by analysis, it is pumped into the acid storage tanks, the second tank is emptied into the first, and fresh lime is added to the second. The process of absorption is then repeated. The composition of the acid liquor varies in different mills and even in the same mill from time to time as the quality of wood varies. A specimen analysis of the liquor, expressed in the mill terms, showed free sulphur dioxide, 2.5 per cent; combined sulphur dioxide, 1.1 per cent; a total of 3.6 per cent. "Free sulphur dioxide" is the total acidity of the solution expressed as $SO_2$. It is therefore the free dissolved gas plus one-half the sulphur dioxide present as bisulphite. The "combined sulphur dioxide" represents the rest of the bisulphite radicle. The actual composition of the liquor is therefore as follows, the total base being regarded as calcium:

*Analysis of sulphite liquor.*

| | Per cent. |
|---|---|
| Calcium (Ca) | 0.7 |
| Sulphur (S) | 1.8 |
| or, in combination— | |
| Calcium bisulphite ($CaH_2(SO_3)_2$) | 3.5 |
| Dissolved sulphur dioxide gas ($SO_2$) | 1.4 |

For one charge of a digester of average dimensions, 12.8 by 34 feet, producing about 7 tons of dry pulp at each "cook," 16,000 gallons of acid liquor are used.

## THE DIGESTER.

The digester consists of an upright steel cylindrical shell with a conical bottom and a nearly hemispherical top, lined with lead, within which is another lining of resistant glazed brick, pointed with a special mortar. Older forms of digesters have concrete linings. The inside dimensions of a digester of average size are, diameter 12.8 feet, total height 34 feet, and its capacity is about 2,700 cubic feet.

## THE "COOK."

About 12 cords of wood chips are first placed in the digester, and then about 16,000 gallons of the acid liquor are run in, filling the digester within 6 feet of the top. The shell is then closed tightly and steam is admitted. The contents are brought rapidly to boiling temperature and then the pressure is raised gradually to about 65 pounds, two hours being consumed in this heating. During the next two hours the pressure is increased more slowly to about 80 pounds. At this point the digester is full of liquor, the water condensed from incoming steam having completely filled the space which was left at the time of filling. In order, therefore, to add more steam it is necessary to "relieve." This process consists in allowing the liquor slowly to escape from the top of the digester as steam enters at the bottom. This relief liquor is strongly acid, and as a rule is returned to the acid-liquor tanks to be used again. There is some objection to such recovery of the relief, because it is rather dark colored and is apt slightly to color the next "cook." The temperature is carefully noted and frequent analyses of the liquor within the digester are made during the "cook," especially during the last two hours. Small samples for analysis are drawn from a tap in the side of the digester near the top. They are examined for total sulphur dioxide and the color and odor are noted. If in the opinion of the attendant the reaction is proceeding too fast, the incoming steam and the relief are both shut off and the "cook" is "held." It is intended to complete the "cook" in about six hours. Nearly at that time the sulphur dioxide content begins suddenly to fall, the color becomes darker, and a peculiar characteristic odor develops. The reactions at that time are proceeding very rapidly and the charge must be blown immediately or a dark-colored stock will result. The skill of the operator is here well shown in bringing about this rather sharp end point at almost the exact time desired, six hours. A large blow-off valve is then opened at the bottom of the digester and its entire contents are blown under full pressure into the blow pit, which is a large covered wooden tank, 22 feet in diameter and 20 feet deep, provided with a large air shaft for the escape of the steam and gases. Opposite the end of the pipe leading from the digester there is a bronze baffle plate, against which the contents of the digester are thrown with great force. The pit is provided with a false bottom and the liquor is rapidly drained off. It is essential at this point to remove all the acid liquor as rapidly as possible. After the blowing the liquor darkens rapidly from a light-garnet shade to nearly black, and its retention in the pulp results in a dark-colored product. About 15,000 gallons of wash water are added as soon as possible and drained off. A second washing is then given with the same amount of water, when the drains are closed, more water is added, and the stock is ready to be pumped to storage tanks. A small amount of the acid liquor is taken out during the "cook" as relief, but the principal part of it is discharged at the end of the "cook," constituting the sulphite pulp waste liquor.

## SCREENING AND WASHING THE STOCK.

The two processes of screening and washing the stock are carried on simultaneously, and can best be described together. The stock is pumped from the blow pit into storage tanks, from which it is pumped as fast as needed into an elevated tank, flowing thence to the screens and the washing machinery. It first passes through a long revolving cylindrical screen, slightly inclined from the horizontal and provided on the inside with a continuous worm-shaped vane. This screen is very finely meshed, and its function is to remove a large part of the water from the stock. Next the stock passes into a similar cylinder with rectangular meshes about one-fourth of an inch wide and 1 inch long. The wood fiber is washed through these meshes by the aid of a stream of water playing from above. All knots and undigested chips are retained in this screen, collected at its open end, and measured, the amount and character of the undigested portions being regarded as a valuable criterion of the care with which the preceding processes have been conducted. On the average, there will be about 4 cubic feet of this material per "cook," or a little over half a foot per ton of dry pulp. The stock passes from these screens to the settling tanks or "rifflers," long troughs about 6 feet wide and 2 feet deep, provided with baffles on the bottom for the retention of sediment. The object of the tanks is to remove by sedimentation any sand or grit which may have gained access to the stock from the machinery or otherwise. The stock is now ready for the final screening, by which it is separated into marketable stock and tailings. The tailings from the first screening process are generally run through a second screen and a little good fiber is saved in that way. The final tailings are passed over a wet machine and felted into low-grade pulp, which is sold for use in the manufacture of leather board. The screened pulp also is passed over a wet machine, which is essentially a revolving screen that separates the bulk of the water from the pulp, leaving the latter in a rather thick sheet. If the pulp is to be sold or used as unbleached pulp, it is taken from the wet machine at this point, passed between large wooden rollers, and finally removed in the form of thick sheets of wet pulp. If it is to be bleached, it is removed mechanically from the rolls of the wet machine, mixed with a large volume of water, and conducted to the bleach tanks.

## BLEACHING THE STOCK.

The unbleached pulp as it comes from the wet machine has a very slight brownish color, although it appears pure white to the inexperienced eye. If such pulp is made into paper, however, it is likely to darken rapidly with age and drying, so that pulp for high-grade papers must be bleached with chloride of lime. Commercial chloride of lime, or bleaching powder, consists mainly of calcium hypochlorite, and it is made by passing free chlorine gas over quicklime. The trade name, chloride of lime, is therefore a misnomer. A typical analysis, by Wagner,[a] of bleaching powder of good quality is given herewith:

*Analysis of chloride of lime.*

| | |
|---|---|
| Calcium hypochlorite ($2CaOCl_2+H_2O$) | 82.65 |
| Calcium carbonate ($CaCO_3$) | .95 |
| Calcium chloride ($CaCl_2$) | .44 |
| Calcium hydrate ($Ca(OH)_2$) | 6.80 |
| Water ($H_2O$), free | 9.82 |
| | 100.66 |

Inasmuch as the chlorine alone of the hypochlorite is available for bleaching purposes, a sample of bleaching powder having the above analysis would contain 43 per cent of "available" chlorine and would be called a 43 per cent bleach. The product on the market seldom contains so much chlorine as that, good grades in this country running from 35 to 40 per cent available chlorine.

The bleaching powder, or "bleach," as it is called in the mill, is received in large iron casks, each holding about 600 pounds. They are emptied into a mixing tank with approximately 3 gallons of water to a pound of bleach. Generally, an ordinary tank provided with a rotary agitator is used for this mixing, but at the Mechanicsville mill an improved mixer is in service, which appears to be very efficient. The tank is conical in shape, about 15 feet high and 10 feet in diameter at the top, tapering to a point at the bottom. A centrifugal pump with a 3-inch discharge is near the tank at its bottom level. This pump withdraws the liquid mixture from the bottom of the tank and discharges it horizontally into the upper part in a direction tangential to the periphery. Circulating the liquor through the tank in this manner produces an immense vortex, so that, although the liquor whirls about the sides of the tank to the level of the inlet, one can look down into this vortex almost to the bottom of the tank. This process accomplishes a thorough mixing of bleach and water in a comparatively short time. The mixture then flows into a large brick

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[a] Wagner, R. von, Manual of chemical technology; trans. from 13th German ed. by Sir William Crookes, New York, reprint of 1904, p. 360.

settling tank and is allowed to settle until a clear liquor can be decanted. This liquor is tested for strength with a Baumé hydrometer and is mixed with the proper amount of a weak bleach extract to give it the required strength of about 3° B. This weaker solution is made by a second extraction of the sludge or "grout" remaining after the first decantation. The grout is usually strengthened by the addition of a small amount of fresh bleach, agitated with a fresh supply of water, and again submitted to sedimentation. The liquor obtained constitutes the weak bleach mentioned above, while the sludge remaining, the "second grout," is agitated a third time with fresh water and again settled. The third lot of supernatant liquor constitutes the water used in the first extraction of a new lot of bleach; the "third grout" is a waste product. Reference to the analysis already given will show that it consists essentially of calcium hydrate, with more or less carbonate of calcium and other impurities derived from the original lime from which the bleaching powder was prepared.

The bleach solution of about 3° B. is mixed with pulp in the proportion of about 30 gallons of solution to 100 pounds of pulp.[a] The mixture is passed successively through a series of tanks, eight in number, in which it is brought to and maintained at a temperature of about 100° F. and is mechanically stirred. Tests of this mixture are constantly being made as it passes from each tank to the next, and additional bleach solution is added as required, the processes being so regulated that, after the complete treatment, requiring about six hours' time, the pulp will be satisfactorily bleached and the bleach will be exhausted as completely as possible. It is next necessary to wash out of the pulp mixture the residual bleach and the calcium chloride resulting from the process. This is accomplished by first passing the stock under a series of washers. A washer is essentially a frame, in the form of an eight-sided prism, covered with fine-meshed copper gauze, and mounted on a horizontal axis, so that it is about half submerged in the pulp. It rotates slowly in the direction of the moving stream of stock, and as the water passes through the gauze it is collected in buckets suitably arranged within, elevated to a position above the center line of the box, and discharged through a side outlet. By this means a considerable volume of water is separated from the stock. Fresh water is admitted after each treatment and the washing is repeated several times, after which the washed stock is passed over a wet machine as previously described. It is then either pressed into sheets of wet pulp or, if it is to be used at once in the mill, is removed from the rolls by a stream of fresh water and run directly to the paper mill.

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[a] All references to pulp in these processes are to the actual weight of air-dry pulp in the mixture, though the pulp is always mixed with a considerable amount of water throughout the process of manufacture.

### SUMMARY.

The various processes described in the foregoing pages have been arranged for convenient reference in diagrammatic form in Plate I. The raw materials that enter into the process are shown along the top line of the diagram in capitals. They are wood, lime, sulphur (or pyrite), bleaching powder, and water. Arranged vertically at the left is a list of the waste and by-products of the process, namely, bark, sawdust, knots, sulphite waste liquor, sand and grit, and sludge or grout from the bleach-solution tanks. Much of the water used in the later processes is returned and used for washing the freshly cooked pulp, so that practically the only liquid waste is the waste acid liquor and the first wash waters, these together making up the sulphite waste liquor. At the bottom of the diagram the finished products of the process are shown, namely, low-grade unbleached pulp and bleached sulphite pulp. Disposal of the grout involves no serious difficulties. It is usually discharged into low-lying fields or into artificially constructed basins, where it is converted into compact masses of carbonate of lime. The small amount of chip dust is readily used in ice houses or as a bedding material for horses. The bark if removed at the mill is either burned or given away for fuel, though it is generally more economical to have the barking done before shipment. In the study of stream pollution, therefore, consideration need be given only to the combined waters resulting from the digestion of the chips and the subsequent washings of the pulp—that is, the liquor here called the sulphite pulp waste liquor.

## SULPHITE PULP WASTE LIQUOR.

### PREVIOUS INVESTIGATIONS.

This waste, arising as it does from an industry involving elaborate chemical methods and necessarily employing skilled paper-mill chemists, has probably received more careful and systematic study than any other waste product of the present day. A prize of 10,000 marks was offered in Germany in 1894 for the best method of preventing the pollution of streams by sulphite liquor, but it still remains unawarded. Scores of processes for utilizing or purifying the waste have been patented in Germany, England, and the United States, but none of them has been sufficiently successful to relieve, in any noticeable degree, the burdensome situation. Technical literature contains reports of exhaustive researches on the constitution of the organic substances found in this liquor, but there is no satisfactory agreement on this point. No more striking commentary on the difficulty of the problem can be made than the bare statement that, in spite of all these researches, the substance is still classed as a waste product. According to Cross and Bevan,[a] who summarize a paper by H. Seidel,[b] no satisfactory application of this by-product has yet been evolved. Evaporation and combustion involve losses of sulphur.[c] A more complete regeneration of the sulphur has been the subject of a series of patents.[d] The process of V. B. Drewson[e] consists in heating with lime under pressure, yielding calcium monosulphite. The sulphite is redissolved as bisulphite by treatment with sulphurous acid. This process is relatively costly, and yields necessarily an impure lye. It has been proposed to employ the product as a foodstuff both in its original form and in the form of benzoate;[f] but its unsuitability is obvious from its composition. A method of destructive distillation has been patented. Seidel,[g] however, found on investigating the process that the yield of useful products is much too low for its economical development. Fusion with alkaline hydrates for the production of oxalic acid[h] is also excluded by the low yield of the product. The application of the liquor to tanning purposes[i] appears promising from the fact that 28 per cent of the dry residue is removed by digestion with hide powder, but this application has been investigated without practical success. Various probable uses are suggested by the viscosity of the evaporated extract, but as a substitute for glue it has proved of little value. It is also used to some extent as a binding material in the manufacture of briquets and as a substitute for gelatine in the petroleum industry. Cross and Bevan[j] and Mitscherlich[k] precipitate a compound of the lignone complex and gelatine by adding a solution of the latter substance to the sulphite waste liquors. The compound is redissolved in weak alkaline solutions and employed in this form for engine-sizing papers. Ekman has patented a process[l] for "salting out" the lignone sulphonates, the product being resoluble in water and the solution having some of the properties of a solution of dextrin. Owing to its active chemical properties this product, "dextron," has a limited capability of being substituted for dextrin. The suggestion to employ the evaporated extract as a reducing agent in indigo dyeing and printing has also proved unfruitful. Seidel's application of the soda salt of the lignone sulphonic acid as a reducing agent in chrome-

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[a] Researches on cellulose, 1895-1900, p. 150.

[b] Zeitschr. angew. Chemie, 1900.

[c] German patents Nos. 74030 and 83438; also Seidel and Hanak, Mitt. Techn. Gew. Mus., 1898.

[d] German patents Nos. 40308, 69892, 71942, 78306, and 81338.

[e] German patent No. 67889.

[f] German patent No. 97935.

[g] German patent No. 45951.

[h] German patent No. 52491.

[i] German patent No. 72161.

[j] British patent No. 1548, 1883.

[k] German patents Nos. 93944 and 93945.

[l] German patent No. 81643.

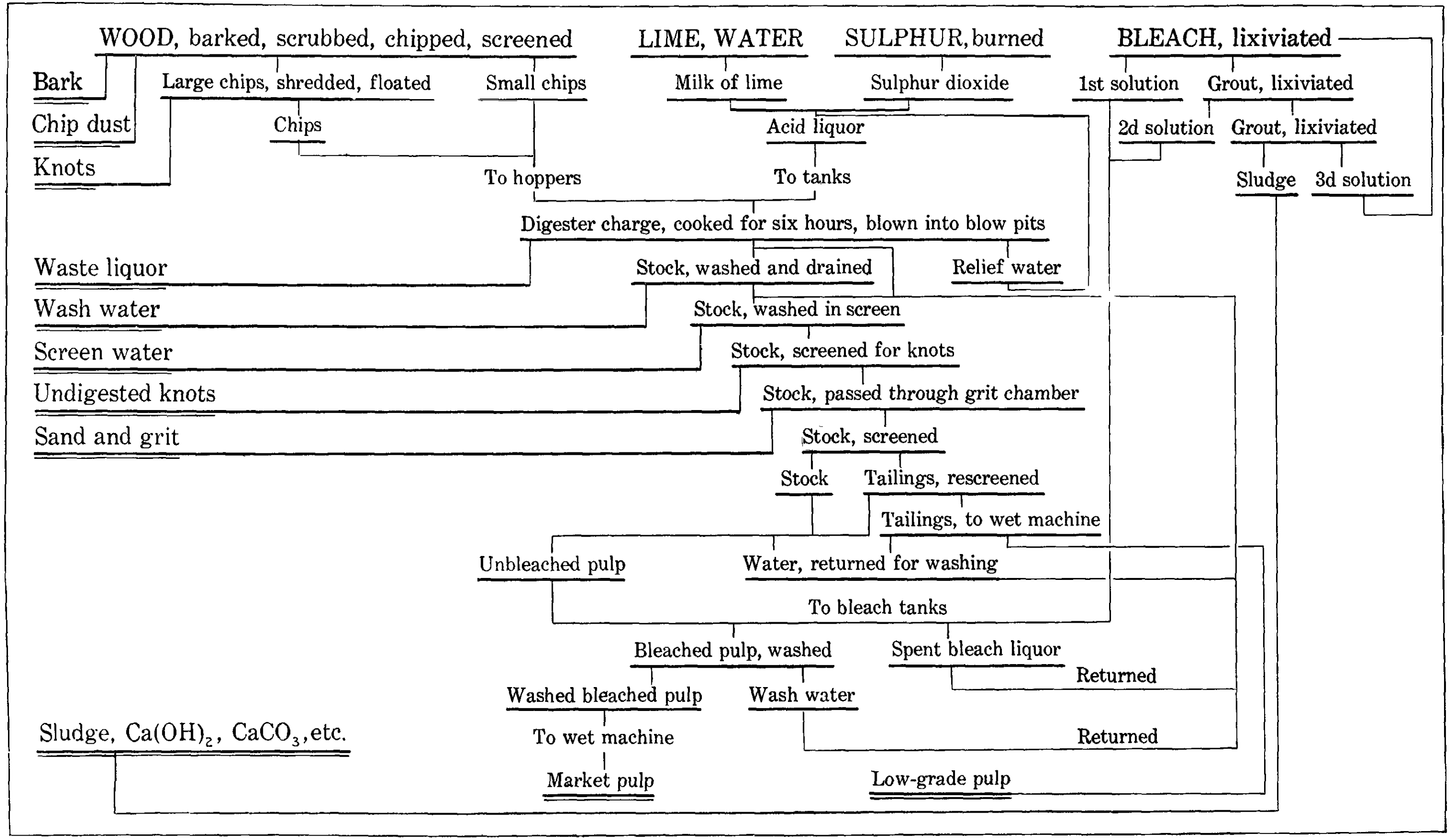

DIAGRAM ILLUSTRATING THE STEPS IN THE MANUFACTURE OF WOOD PULP BY THE SULPHITE PROCESS.

mordanting wool and woolen goods[a] is more successful in practice, and its industrial development shows satisfactory progress. The product is known as "lignorosin." In another place, however, Cross and Bevan[b] comment on this process by calling attention to the fact that such use for a by-product, produced in such enormous quantities, is of relatively small importance.

It is remarkable that the main by-product of the bisulphite process is still for the most part an absolute waste, notwithstanding the many investigations of technologists and attempts to convert it to industrial use. As it represents a percentage of the wood pulped equal to that of the cellulose obtained, it is a waste of potentially valuable material that must be termed colossal. Moreover, as a waste to be discharged into watercourses, it becomes a source of burden and expense to the manufacturer, and with the increasing restrictions on the pollution of rivers it constitutes in many localities a problem to be solved only by the cessation of the industry. The alternative in such cases is dealing with it destructively—that is, by evaporating and burning it. In this treatment the high calorific value of the organic matter appears on the credit side; but, as calcium and magnesium bisulphites are used, the residue from calcination is practically without value. If, however, a soda base is substituted, the alkali is recoverable in such form as to be directly available for the alkaline-sulphide or Dahl process. As a more complicated alternative the soda can be recovered by the old black-ash or Leblanc process, and the sulphur by the now well-established Chance process, in which lime must be added to the concentrated liquors before calcination. The engineering features of the system in respect to evaporating and calcining are the same. Economic working requires (*a*) evaporation by multiple effect and (*b*) calcining on the continuous rotary principle. For the latter process the draft of air is concurrent, by a special device, with the movement of the charge in the furnace, a feature by which a progressively increasing temperature within the furnace is procured. This interesting development has been elaborated by Drewson and Dorenfeldt, to whose publications readers who wish to inform themselves in detail in regard to these developments are referred. The present necessity of a destructive treatment of the sulphite waste liquor being assumed, their scheme has many advantages; sodium bisulphite liquors are more economically prepared and the pulp obtained is superior in paper-making quality and in economy of bleaching to that resulting from the calcium or magnesium bisulphite processes. The soda may be recovered in a form in which it is immediately available as a powerful hydrolyzing alkali in the

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[a] German patent No. 99682.

[b] A text-book of paper making, 2d ed., 1900, p. 143.

manufacture of soda pulp, so that these two systems become complementary to one another. The employment of soda as the base also affords a new motive for developing the electrolytic processes of decomposing salt.

Cross and Bevan's comments present an excellent summary of conditions at the close of 1900. Significant of more recent developments in the methods of utilizing or disposing of this waste is the fact that in their second volume of "Researches,"[a] a treatise purporting to review all work of importance on cellulose industries during the years 1900–1905, these authors make no mention whatever of the sulphite waste problem.

## AMOUNT OF WASTE PER TON OF PULP.

It is now practicable to inquire more carefully into the amount of the waste and its general characteristics. The important facts to be considered in any discussion of stream pollution are the amount and the character of the polluting material independent of the amount of water in which it may be carried. Chemical analyses of the waste liquor in connection with accurate determinations of its volume would furnish the requisite information, and such procedure is usually adopted. In the present case, however, it happens that the amount of polluting material bears a definite relation to the total product of the mill in pulp, independent of slight modifications of the process, whereas the amount of diluting water varies greatly in different mills and even from time to time in the same mill. For example, some mills use the old-fashioned rotary digesters, in which it is not necessary to use more than half the amount of water in the acid liquor that is used in upright digesters. The washing process is often conducted at places where water is plentiful, with a total disregard of economy in water, while in other mills strict economy of water is necessary; therefore the concentration of the waste liquors may be three or four times as great in one case as in another. In view of these facts and of the statement made above, that a definite amount of polluting material is produced for each ton of pulp turned out, it appears that the best procedure is to determine the definite relationship between the amounts of pulp and solid waste. Results obtained at one mill are applicable to any mill using a similar process, though the actual volumes of the wastes may be greatly different. After having determined this fundamental relation, it is of interest to compare the figures obtained with actual analyses of the waste liquor. Such comparison will give an approximate measure of the volume of diluting water.

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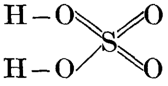
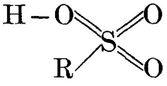
[a] Researches on cellulose, 1900–1905.

A cord of spruce wood ordinarily handled at the mill will weigh about 3,600 pounds, of which about 55 per cent, or 2,000 pounds, is actual wood substance, the remaining 45 per cent being water. The amounts of chip dust, knots, etc., which are really insignificant as compared with the total weights, may be neglected in this calculation. About 1,100 pounds of so-called "air-dry" pulp having 10 per cent water, or, roughly, 1,000 pounds of actually dry pulp, is made from 1 cord of wood. Therefore the production of 1 ton of pulp is accompanied by the production of an equal amount of waste organic material that is discharged in the waste liquor. According to the analysis on page 10, the sulphite liquor contains 0.7 per cent of calcium and 1.8 per cent of sulphur, equivalent, respectively, to 0.058 pound and 0.150 pound per United States gallon. On the basis of 16,000 gallons of acid liquor to a digester charge, which produces 7 tons of air-dry pulp, each ton of pulp is represented by 132 pounds of calcium and 343 pounds of sulphur. About 0.1 per cent of sulphur dioxide, or 9 pounds of sulphur per ton of pulp, is left unoxidized at the end of the "cook." Of the remaining 336 pounds of sulphur 10 per cent may be allowed for loss of free sulphur dioxide in the relief, leaving approximately 300 pounds of sulphur which has been oxidized in the process. The first product of this oxidation is probably sulphuric acid, according to the following equation, the oxygen being derived from the wood during the digestion:

$$SO_2+O+H_2O=H_2SO_4.$$

This presents the simplest idea of the digestive action. Sulphurous acid is oxidized to sulphuric acid with a corresponding reduction of the wood substance. The fate of the sulphuric acid thus formed has not been satisfactorily determined. It is known that in the final product there is little free sulphuric acid. The first effect of its formation would be the precipitation of calcium sulphate, probably on the wood fibers. As magnesium sulphate is soluble, this is probably the reason why dolomitic lime gives such excellent results. If, however, all the calcium or magnesium originally used were converted to sulphate, there would be needed for that reaction only 100 pounds of sulphur, leaving still 200 pounds of sulphur unaccounted for. It will be shown when the chemical nature of the waste is considered that, according to prevailing views, the sulphuric acid from this amount of sulphur again reacts with a portion of the wood substance to form a so-called sulphonic acid. This may be regarded as sulphuric acid in which one of the OH groups has been replaced by an organic radical (R) thus:


Sulphuric acid.


Sulphonic acid.

This reaction is not complete and a small amount of sulphuric acid is generally left in the liquor. For the present it will not be necessary to discuss the relative amounts of these two acids. The waste material resulting from the digestion of sufficient wood to make 1 ton of pulp may be summarized as follows:

*Materials in the waste liquor per ton of pulp.*

| | Pounds. |
|---|---|
| Wood material | 2, 000 |
| Calcium sulphate | 449 |
| Sulphur dioxide (omitted from total) | 18 |
| Sulphur in sulphuric acid and in organic combination | 196 |
| Total solid matter | 2, 645 |

## CHEMICAL COMPOSITION OF THE WASTE LIQUOR.

As has been stated, the actual strength of the waste liquor is entirely a matter of dilution. The 16,000 gallons of acid liquor used in the "cook" producing 7 tons of air-dry pulp is usually diluted with one to two times its volume of water in the blow pit, and other wash waters later mingle with this liquor in the drains. For the purpose of study, however, it is advisable to procure samples of the undiluted waste liquors directly from the digester, because in any plan for the recovery of this liquor it will undoubtedly prove advantageous to separate the undiluted liquor. For the investigation here reported samples of the liquor were collected from the bottom of the digester just before blowing. The hot liquor was drawn into a barrel, allowed to cool, and then bottled in carboys for future use. The subjoined table gives analyses of this liquor and the figures of several analyses of similar liquors by other chemists.

*Analyses of sulphite pulp waste liquor.*

[Grams per liter.]

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. |
|---|---|---|---|---|---|---|---|---|---|
| Total solids | 95 | 82 | 88 | 85 | 93 | 92 | 109 | 52 | 64 |
| Loss on ignition | 82 | 68 | 75 | 69 | 81 | | 90 | 45 | 56 |
| Ash | 13 | 14 | 13 | 16 | 12 | | 19 | 17 | 8 |
| Analysis of ash: | | | | | | | | | |
| Calcium (Ca) | 2. 2 | | | | | | 6. 9 | 1. 76 | 2. 08 |
| Magnesium (Mg) | 1. 2 | | | | | | . 18 | . 97 | 1. 26 |
| Sulphur (S) | 2 | | | | | | | | |
| Total sulphur | 10. 5 | | | | | 9. 2 | | | |
| Free sulphur dioxide ($SO_2$) | 1 | 2. 6 | 2. 2 | 2. 9 | 2. 6 | 3. 8 | | . 94 | . 90 |
| Sulphite radicle ($SO_3$) | | 7. 3 | 7. 9 | 6. 7 | 1. 2 | 3. 8 | 3. 8 | 1. 10 | 1. 36 |
| Sulphate radicle ($SO_4$) | | 4. 1 | 5. 4 | 4. 8 | 2. 7 | 1. 9 | 7. 2 | [a]9. 27 | [a]11. 10 |
| Oxygen consumed | 36 | 52 | 52 | 50 | 60 | | | | |
| Specific gravity | | | | | | | | 1. 024 | 1. 028 |

[a] Exclusive of the organic S.

No. 1, by the writer, is the average of two analyses of waste liquor collected directly from the digester at the Mechanicsville mill. Nos. 2 to 6, inclusive, are quoted by Hoffmann,[a] Nos. 2, 3, 4, and 5 being

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[a] Hoffmann, C., Practisches Handbuch der Papier Fabrikation, Berlin, 1897.

by Wickelhaus,[a] and No. 6 by Lehman. No. 7 is given by Schubert,[b] and Nos. 8 and 9 are taken from the notebook of S. C. Lindberg, paper-mill chemist, who has kindly permitted their use.

These analyses give an excellent idea of the general character of the liquid. The proportions of the various constituents are in agreement with the figures which have been calculated from the amounts of raw materials used. The analyses also determine satisfactorily the nature of the inorganic matter in the waste and show the relatively large amount of organic matter present, about 80 per cent of the total solids.

## CHEMICAL NATURE OF THE ORGANIC MATERIAL.

Thus far only the total amount of waste material in the liquor resulting from the digestion of 1 ton of dry pulp and its division into organic and inorganic constituents have been considered. The chemical nature and the essential characteristics of the organic matter deserve further consideration. Though our knowledge of the chemistry of wood is not extensive, the following facts seem to be definitely settled and may be accepted as embodying all that is positively known. The wood substance itself, freed from the relatively small amount of intercellular matter, such as gums and sap constituents, is a homogeneous material of fairly constant composition. To this substance chemists have given the name ligno-cellulose. Lignocellulose can be broken down by suitable chemical treatment into two or more substances. These are cellulose, which is the material of the wood pulp, and a complex substance or mixture variously called lignose, lignin, or lignone. It is this latter body or mixture of bodies which in the sulphite process is supposed to be sulphonated, giving rise to a substance known as lignon-sulphonic acid. The constitution of this substance is not known, nor is its chemical identity even assured. Beyond these meager facts all is hypothesis, despite the large amount of experimental work which has been done on the substance under discussion. Probably the best estimate of the character of lignone is given by Cross and Bevan,[c] who made an exhaustive study of the subject.

They conclude that it is a single substance made up of (*a*) $2C_{18}H_{18}O_{10}$, a ketone transitional to quinone which chlorinates directly to marriogallol; (*b*) $6C_5H_4O_2$, furfural, in combination by condensation with (*a*) and (*c*); and (*c*) $5C_2H_4O$, acetic residue. The simplest empirical formula for their lignone is $(C_6H_6O_3)n$, *n* being not less than some

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[a] Papier Zeitung, 1895, No. 38.

[b] Schubert, Max, Die Cellulose Fabrikation, Berlin, 1892.

[c] Cross, C. F., and Bevan, E. J., Contributions to the chemistry of lignification: Jour. Chem. Soc., vol. 15, trans., 1889, p. 199.

multiple of 24. Tollens[a] gives as the result of his analysis of the sulphonated form the empirical formula—

$$C_{24}H_{23}O_7(OCH_3)_2.(SO_3H).$$

This formula must be slightly modified in view of Cross and Bevan's satisfactory determination of the presence of 5 acetic residues in the $C_{76}$ molecule, instead of 6, as given by Tollens's formula. It has been stated that the chemical identity of the sulphonated form has never been satisfactorily shown. The experimental work on sulphite liquor, conducted by the author, seems to prove that the substance in question is probably not a true sulphonic acid.

## PURIFICATION OF SULPHITE WASTE LIQUOR.

Investigations on the disposal of waste liquors may be carried out either with the object of recovering and utilizing the material contained therein or with the simpler aim of purifying the liquid so that it may safely be discharged into a stream. The former method of investigation has appealed most strongly to manufacturers and chemists, and a great many attempts have been made to discover some useful by-product in the waste sulphite liquors. Reference to these investigations will be made later. Owing to the failure in general of all such attempts and to the stringent laws against stream pollution, particularly in Germany, some attempts have also been made simply to purify the liquor by precipitating the organic matter, the experiments having no reference to the recovery of valuable by-products. One of the earliest of these investigations was made by H. Frank,[b] who gives the following composition of the sulphite waste which he used:

*Composition of sulphite waste.*

| | Grams per liter. |
|---|---|
| Total solids | 82 |
| Loss on ignition | 59 |
| Ash | 23 |
| Calcium (Ca) | 5.3 |
| Magnesium (Mg) | .25 |
| Sulphate radicle ($SO_4$) | 14.4 |

In the process developed by Frank the liquor is treated first with lime to neutralize the free acid and then with chimney gases to carbonate the excess of lime and oxidize the calcium sulphite. A heavy precipitate of sulphate and carbonate is formed and it is claimed that much of the organic matter is dragged down, so that the supernatant liquid could be discharged into the stream. This process was later investigated more thoroughly by F. B. Ahrens, E. Klingstein, and P. Schubert,[c] who state that many German wood-pulp

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[a] Quoted by Cross and Bevan, Researches on cellulose, p. 126.

[b] Wien. Jahresbericht, 1887, p. 1177.

[c] Zeitschr. angew. Chemie, 1895, p. 41.

mills have been compelled to close because it was found impossible to comply with the requirements of rivers-pollution officials. The examination of the waste sulphite liquor which they used showed that it gave a strongly acid reaction, had a specific gravity of 1.0465 at 15.8° C., and was optically inactive. The dry residue was 9.4 per cent, of which 1.11 per cent was ash and 8.29 per cent organic matter—not strictly accurate determinations. The liquors from the digesters were nearly neutralized by passing them over limestone. The hot lye was then mixed with a known quantity of fresh lime water once boiled, filtered, and the filtrate neutralized with carbonic-acid gas. The results obtained are shown in the following table:

*Results of experiments in neutralizing hot sulphite waste liquors.*

| CaO added. | Analysis of supernatant liquor. | | |
|---|---|---|---|
| | Dry substance. | Ash. | Organic matter. |
| *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 2 | 8.75 | 1.80 | 6.95 |
| 3 | 7.48 | 1.59 | 5.89 |
| 4 | 7.36 | 1.71 | 5.65 |
| 5 | 7.13 | 1.56 | 5.57 |
| 6 | 6.86 | 1.52 | 5.34 |
| 7 | 6.74 | 1.58 | 5.16 |
| 8 | 6.65 | 1.54 | 5.11 |
| 9 | 6.61 | 1.57 | 5.04 |
| 10 | 6.79 | 1.51 | [a] 5.28 |
| 11 | 6.54 | 1.55 | 4.99 |
| 12 | 6.52 | 1.49 | [a] 5.03 |
| 15 | 6.31 | 1.49 | 4.82 |
| 20 | 7.00 | 1.60 | [a] 5.40 |
| 30 | 4.99 | 1.01 | 3.98 |

[a] Organic matter rendered soluble again by boiling.

When the liquors were treated cold, the following results were obtained:

*Results of experiments in neutralizing cold sulphite waste liquors.*

| CaO added. | Analysis of supernatant liquor. | | |
|---|---|---|---|
| | Dry substance. | Ash. | Organic matter. |
| *Per cent.* | *Per cent.* | *Per cent.* | *Per cent.* |
| 2 | 6.21 | 1.11 | 5.10 |
| 3 | 6.19 | 1.33 | 4.96 |
| 4 | 5.26 | 1.00 | 4.26 |
| 6 | 5.08 | 1.04 | 4.04 |
| 8 | 4.96 | 1.10 | 3.86 |
| 10 | 5.67 | 1.22 | 4.45 |
| 12 | 5.76 | 1.23 | 4.53 |
| 14 | 6.26 | 1.29 | 4.97 |

Sodium aluminate was also tried as a precipitant, but the results were less satisfactory. The precipitated and neutralized liquors were then treated electrically. A current of 5 amperes and only sufficient potential was passed through the liquid between platinum electrodes, but no diminution in either mineral or organic matter was observed after two hours. A high-tension current (106 volts) was then tried, but the results were equally ineffective after a test of the same duration. It is evident, these authors conclude, that the objectionable organic matter, if removable at all, calls for some process hitherto undiscovered. Ahrens tried, unsuccessfully, to treat this waste bacterially after neutralization on the lines of his patent. It was found absolutely sterile to begin with, and the amount of bacterial filtration required for its decomposition was altogether impracticable. E. Bruch[a] found that if the waste liquors are treated when acid, or neutral, with leather glue, a compound of tannic acid and glue is formed which coagulates on storing and becomes highly viscid. If then the clear, colorless top liquor is decomposed with aluminum sulphate, another gummy precipitate is formed. Both precipitates are soluble in alkalies and in weak ammonia, and may be removed, dried, and powdered. If the clear liquor is then neutralized with chalk or lime, a precipitation and clarification ensue, and the top liquor is free from smell and has lost about 25 to 30 per cent of the total organic constituents, and these the most easily decomposable.

## UTILIZATION OF SULPHITE WASTE LIQUOR.

By far the most important work on this waste liquor has had for its object the utilization of the organic matter. Its complex chemical nature and relatively large amount and the fact that it is still a chemical mystery make the field particularly inviting for research. In some interesting laboratory experiments made by Buddens,[b] and quoted by Griffin and Little,[c] the waste liquor was neutralized by ammonia, the lime was precipitated by ammonium carbonate, and the carbonate of lime thus formed was separated by filtration. The dark-brown filtrate was evaporated and the dried residue distilled. The dried residue contained 7.2 per cent of ammonia as salts. Water and a yellow oil were obtained in the condenser, and finally a crystalline sublimate appeared on the walls of the tube. The escaping gases were caught in a gasometer. The oil had at first a mercaptan-like odor, but this disappeared on heating slightly. The odor was without doubt due to organic sulphur compounds, which were present in traces. The mixture of oil and water was, after this heating, distilled with steam, the distillate was shaken out with ether and then dried, and the ether was evaporated over calcium chloride. The brown oil that remained boiled at 130° C., and as it colored a pine chip moistened with hydrochloric acid a strong

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[a] Die Abwässerreinigung der Cellulose-Fabriken und die Papierleimung: Chem. Zeitung, 1892, p. 1782.

[b] Buddens, W., Papier Zeitung, March, 1891.

[c] Griffin and Little, Chemistry of paper making, New York, 1894.

carmine, it was believed to be pyrrol. Pyrocatechin was also found in the distillate, as was proved by color tests with iron salts and by the reduction of Fehling's solution. The gases from the first distillation were carbon monoxide, hydrogen, marsh gas, and hydrogen sulphide. Four hundred grams of the residue yielded 180 grams of coke, 30 liters of gas, and 200 grams of distillate. Mucic and saccharic acids could not have been present as such in the liquor, because they are formed by the oxidation of carbohydrates, and the action of the liquor is a reducing one. Yet pyrrol is formed by distilling the ammonium salts of these two acids. The only way of accounting for pyrrol is by considering that succinic acid is formed from the resins in the wood—a not improbable assumption. Ammonium succinate changes readily into ammonium succinamide, which gives pyrrol when it is heated with reducing agents. The presence of pyrocatechin is due to the presence of dioxybenzoic acid (1, 3, 4), which is in the liquor as dipyrotechnic acid. The decomposition of this acid by distillation with ammonia produces tannic acid and pyrocatechin. Doctor Buddens states that there is no tannic acid in the liquor, which will give a blue-black color with ferric chloride, because the tannin in wood is reduced by digesting with sulphurous acid. The reduction is probably due to dipyrocatechuic acid, but by treating the liquor with ammonia and distilling, tannic acid is eventually formed. Sulphites are oxidized to sulphates when the tannin is reduced. It is possible, therefore, that the difficulty of pulping wood rich in tannin by the sulphite process is due to the action of the tannin, which renders the sulphurous acid ineffective. Lindsey and Tollens,[a] in their systematic search for the different sugars, used liquor from a Mitscherlich slow-process cook, with a specific gravity of 1.055, showing total solids 9.5 per cent, and calcium 0.41 per cent. The solution was pale yellow in color and strongly reduced Fehling's solution. They found no evidence of the presence of saccharose, dextrose, or dextrose-yielding sugars, traces only of levulose or levulose-yielding sugars, and but a small amount of galactose. On the other hand, mannose, determined as a hydrazine, was found to represent 6 to 7 per cent of the original total solids. Furfural was found in some quantity on heating with hydrochloric acid, and xylose was identified in the solution. Alcoholic fermentation of the liquor gave amounts of alcohol corresponding to only 1.2 per cent of the total carbohydrates. The remaining gummy mass behaved as a homogeneous complex, yielding several synthetic preparations, the analyses of which were consistent with the view of its homogeneity.

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[a] Liebig's Annalen, No. 267, 1892, p. 341. Abstracts Jour. Chem. Soc., 1892, p. 802.

A summary of various attempts to recover valuable products from the waste has already been given (pp. 15–18). Thus far no satisfactory recovery of valuable chemical substances has been made. The substance itself has been used as a substitute for glue and for sizing. Mitscherlich precipitated the tannin compounds with glue in the presence of alum and sulphuric acid, obtaining a rubbery mass, soluble in weak alkali, which could be used in engine sizing. He later improved the process[a] by precipitating with lime to remove the sulphite present and then diffusing the liquor through membranes. The diffusible portion contained sugars and was fermented for alcohol. The nondiffusible part was treated as described above in order to remove the tannins. A later patent[b] describes a process in which, after the removal of the calcium salts, the liquor is heated with hair or bone to give a semiwaterproof sizing. V. Drewnen and L. I. Dorenfeldt[c] treat the liquor with soda ash recovered from the soda pulp process, precipitating the lime and a part of the organic matter. They draw off the clear liquor and burn the residue, using the heat of the combustion to evaporate more liquor. The liquor is said to contain more calorific energy than is necessary to evaporate it. The soda ash is recovered from the residue by the usual process, and about 60 per cent of the sulphur is recovered by liberating free sulphur dioxide with carbon dioxide gas. The fumes and the gases from the evaporation were found to be very corrosive. This trouble was finally overcome by combining the wastes of the sulphite and soda pulp mills and treating them like soda wastes. Frank's process, as described by Schubert,[d] consists in precipitating the remaining calcium bisulphite as normal sulphite with excess of lime, after which the precipitate is redissolved in an excess of sulphur dioxide. Such treatment would recover only a small part of the total sulphur. Meyer's process, also described by Schubert,[e] seeks to recover valuable products by destructive distillation of the organic material in the waste. The liquors are neutralized, concentrated to a thick sirup, mixed with charcoal to a paste, and distilled. The yield of valuable products is too small to make the process economical. H. Seidel has employed the soda salt of the lignone sulphonic acid as a reducing agent in chrome mordanting wool, where, under the name "lignorosin," it is used in place of tartaric and lactic acids.[f] The material, especially when concentrated, is very sticky, and many attempts have been made to utilize it as a substitute for glue. In J. S. Robe-

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[a] United States patent No. 681241, 1901.

[b] United States patent No. 687844, 1901.

[c] United States patents Nos. 620755, 1899, and 726036, 1902.

[d] Schubert, Max, Die Cellulose Fabrikation, Berlin, 1892.

[e] Op. cit.

[f] Rev. gén. des mat. col., vol. 2, 1898, p. 370. Jour. Soc. Chem. Ind., vol. 17, 1898, p. 1043. British patent No. 19005, 1897. German patent No. 99682, 1897.

son's process[a] for the manufacture of an adhesive, which is being used at Ausable Forks, N. Y., by a large mill,[b] the waste liquor is neutralized with lime and evaporated in vacuo. The product is a thick, molasses-like fluid, which finds application in foundries as an adhesive in core making. C. H. Voight[c] makes a glue substitute by heating starch and a peroxide with the sulphite liquor. A. G. Brooks[d] evaporates the liquid till it contains 20 per cent water, then adds carbohydrates or albuminoids and dries the mass, which is used for fuel, pitch, glue, resin, or size. Knoesel[e] concentrates to 25° B. and treats with a slag meal high in phosphorus (Thomas slag). It is claimed that the phosphorus of the slag is rendered soluble in citrates and becomes available in fertilizing. Ahrens[f] investigated the process and could not substantiate its claims. Processes have been proposed for the destructive distillation of the substance, and, as has already been stated, both pyrrol and pyrocatechin have been obtained in this manner. The yield of these products has not been sufficient to make the process successful. Patents have been granted for processes involving the use of the liquor in tannin.[g] According to Seidel[h] 28 per cent of the solids are removed by rawhide powder. No satisfactory method has yet been described for separating the tannin substance from the remainder. This seems to be one of the important lines for future investigation. Morterad[i] subjects the hot liquors to a partial vacuum and removes from them a considerable volume of sulphur dioxide. Bergerhopf[j] made a cheap grade of paper for newspapers by using the waste liquors to digest sawdust. Eckman[k] "salts out" the liquors and makes a concentrated solution, which he calls "dextrone," a substitute for dextrin, or British gum.

## EXPERIMENTAL INVESTIGATIONS WITH THE ORGANIC MATERIAL.

The knowledge of the chemical reactions which characterize lignone is very meager. Early in the present study it was deemed important to obtain additional light on the general behavior of this material. It was hoped that in this way knowledge of its chemical nature might be enlarged and particularly that some reactions of industrial value

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[a] United States patent No. 833634, 1906.

[b] Paper Trade Journal, Jan. 5, 1905, p. 12.

[c] United States patent No. 770202, 1904.

[d] British patent No. 8088, 1901.

[e] Jour. Soc. Chem. Ind., 1902, p. 489.

[f] Chem. Zeitung, vol. 4, 1905, p. 40. Chem. Centralbl., vol. 1, 1905, p. 700. Jour. Soc. Chem. Ind., vol. 14, 1905, p. 343.

[g] German patent No. 72161.

[h] Zeitschr. angew. Chemie, 1900, p. 951.

[i] United States patent No. 833936, 1906.

[j] German patent No. 160651, 1903. Jour. Soc. Chem. Ind., vol. 24, 1905, p. 1028.

[k] German patent No. 81643.

might be discovered. For this study preparations of the dry material were made in various ways; the solubility of these preparations was investigated; attempts were made to identify a sulphonic acid in the material; and various other reactions were studied.

## PREPARATION OF CRUDE "LIGNONE."

Three different preparations of the dry material were used. "Lignone A" was obtained in dry form at the mill. It was observed that certain steam pipes passing near the blow pit were heavily coated with a hard vulcanite-like substance, nearly an inch thick in places. About a pound of this material was chipped off and used in certain of these experiments. "Lignone B" was the supposed calcium compound obtained by evaporating the liquor to one-half volume and salting out with common salt. A granular amorphous substance, containing some salt and moisture, was obtained. "Lignone C" was supposed to be the sodium compound. When the liquor was neutralized with sodium carbonate and allowed to settle, a large amount of calcium carbonate was precipitated. The remaining liquor was evaporated and salted.

## SOLUBILITY OF CRUDE "LIGNONE."

The solubility of each of these preparations was tested with several solvents in an endeavor to obtain a liquid from which the material could be crystallized. No solution took place in either hot or cold benzoin, amyl alcohol, allyl alcohol, petroleum ether, amylene, amyl acetate, aniline, toluene, xylene, nitrobenzene, carbon bisulphide, ethyl ether, or benzol. Benzoin seemed to soften the substance. The tests were repeated after acidifying to see if a free acid could be found which would dissolve, but the results were again negative. The two alcohols dissolved the samples if diluted with water. Ordinary ethyl alcohol also dissolved it, a result probably due to the water present. Absolute ethyl alcohol was not tried.

## REACTIONS WITH PHOSPHORUS CHLORIDES.

An important general reaction of sulphonic acids is that with phosphorus pentachloride, giving sulphon-chlorides according to the reaction—

$$R.SO_2.OH + PCl_5 = R.SO_2.Cl + POCl_3 + HCl.$$

Sulphon-chlorides are for the most part insoluble oils which combine with ammonia to form crystallizable sulphonamides, as follows:

$$R.SO_2.Cl + 2NH_3 = R.SO_2.NH_2 + NH_4Cl.$$

Appropriate mixtures of the crude "lignones" with varying amounts of the pentachloride, the oxychloride, and mixtures of the two were made. No indication of any reaction was obtained at room temperature or at temperatures up to 180° C., at which point the oxychloride begins to distill. Altogether about twenty attempts were made to bring about this reaction. The products after heating were treated with ammonia, but no evidence of any amide was ever obtained. It must be concluded, therefore, that the "lignone" does not react with the chlorides of phosphorus in the way which characterizes sulphonic acids in general.

### FUSION WITH ALKALI.

Another characteristic of sulphonic acids is their ready reduction to corresponding phenols on fusion with caustic alkali according to the reaction—

$$R.SO_2.OH + 2KOH = K_2SO_3 + R.OH + H_2O.$$

Preparations of "lignone" were fused in this way, the resulting masses being extracted with ether and evaporated. Only mere traces of ether extract were obtained, and these gave none of the usual tests for phenols. During the fusion the sulphur gave strong evidence of its escape into the air in the form of some volatile mercaptan, with a very penetrating and sickening odor.

### POSITION OF THE SULPHUR IN "LIGNONE."

As in both series of tests just described the "lignone" failed to react in a way characteristic of true sulphonic acids, the presumption is reasonable that a sulphonic acid is not present. An interesting question is therefore raised. How is the sulphur in this material related to the molecule? In the salting-out experiments some light was thrown on this question. It was found that a considerable part at least of the sulphur was in such loose combination that it was given off as sulphur dioxide in the cold during the salting process. The result when first observed was attributed to the sulphur dioxide in the liquor, but it was possible to show that such was not its origin. A small amount of the fresh liquor was cautiously evaporated nearly to dryness and then diluted with water to the original volume. This solution was then salted in parallel with a fresh solution. As nearly as could be determined by the sense of smell, equal amounts of sulphur dioxide were given off by both samples. Confirmatory results were obtained by dissolving some of "lignone A," a completely dried sample, and treating it in the same manner. That all the sulphur could not be removed by this procedure was evident on drying and igniting the salted sample, when the same disgusting odor was given off as by the original sample and apparently to the same degree. This point was verified quantitatively by titration with iodine solution. When the solution was acidified, an evolution of sulphur dioxide occurred and the reducing power increased from an equivalent of 0.01 per cent to 0.104 per cent of sulphur dioxide. On continued boiling without acid the reducing power increased from 0.011 to 0.015 per cent of sulphur dioxide. Boiling with potassium hydrate still further increased it to 0.201 per cent. Lime water had a similar but less marked effect. All these observations point to the probable fact that a sulphurous ether is present. Such ethers yield sulphur dioxide to sulphuric acid and are readily hydrolyzed by an alkali. The results here obtained are, in all respects, what would be expected from sulphurous ether, and the presence of a sulphonic acid has not been verified. Though the presence of the latter compound has not been disproved, the writer is strongly of the opinion that the major part, at least, of the sulphur is present in the form of an acid sulphurous ether of some complex hydrocarbon radicle.

## REACTIONS WITH AROMATIC AMINES.

Previous investigators have generally agreed that "lignone" possesses aldehydic properties. A characteristic property of aldehydes is that of forming condensation products with certain bodies; the aldehyde and the other substance—aniline, for example—condense to form a complex molecule. When a solution of "lignone" was mixed with aniline, a bright-red precipitate was formed. An excess of aniline changed this body to a black insoluble gum. The reaction took place equally well with aniline oil or with aniline sulphate. All attempts to purify the product failed. It was insoluble in all solvents except acids, which apparently decomposed it into its original constituents. Reference will later be made to the action of strong nitric acid on the gum. Exactly similar condensations were observed with the following: Ethyl aniline, diethyl aniline, dimethyl aniline, methyl diphenylamine, *m*-chloraniline, *p*-chloraniline, dichloraniline (1–2–4), *m*-nitraniline, *p*-nitraniline, *o*-toluidine, *p*-toluidine, dibrom-*o*-toluidine, *o*-tolidine. Substituted amines which did not give condensations were *o*-nitraniline and dinitraniline (1–3–5). Bright-red products were formed in every case where the amine retained the $NH_2$ group. With amines in which substitution had taken place in that group brown or black compounds were formed. The reactions of these preparations with fused sodium sulphide is considered under the caption "Sulphur dyes." As in the case of the aniline condensation product, it was not possible to purify these gummy substances. They were decomposed into the original constituents on treatment with strong acids or generally on heating.

## REACTIONS OF THE AMINE CONDENSATION PRODUCTS WITH NITROUS ACID.

On the assumption that the condensation products still retain their characteristic amine group, they were treated with nitrous acid in an ice bath, in the hope of obtaining some new bodies through the diazo reaction. In the case of aniline this reaction is—

$$C_6H_5NH_2.HCl + NO_2H = C_6H_5N:NCl + 2H_2O.$$

When this substance alone is heated it decomposes, yielding phenol, but in the presence of other substances, such as some unaltered aniline, reactions of technical importance can be brought about:

$$C_6H_5N:NCl + H_2O = C_6H_5OH + N_2 + HCl,$$

or

$$C_6H_5N:NCl + NH_2C_6H_5 = C_6H_5N:N.NHC_6H_5 + HCl.$$

The product of the latter reaction is diazo-amidobenzene, a starting point for the preparation of an important group of dyes. Application of the diazo reaction to the condensation products above described did not generally result in apparent change. In some experiments an excess of the amine reacted in a manner quite characteristic of the amine itself without any substituted groups. The general inertness of these bodies under such conditions leads to the conclusion that substitution takes place in the amido group of the condensation products. This is further verified by the fact previously shown, that all primary amines gave bright-red condensation products, while the others gave brown or black substances.

## REACTIONS WITH NITRIC ACID.

Concentrated nitric acid was found to have a very vigorous action on the dry "lignone" preparation and on the sulphite liquor itself at high temperatures. The organic matter of the dry "lignone" is completely oxidized, chiefly to oxalic acid, in the presence of a sufficient excess of the acid. Nitrous acid fumes are evolved, and the odor of acetic acid can be distinctly detected. The action of nitric acid on the waste liquor is less violent. When a mixture of one part strong acid and ten parts of liquor is warmed, action begins at once. Nitrous and acetic acids are evolved, as with the dry product, and the color of the solution changes from dark brown to bright, golden orange. This solution, after neutralization of the free nitric acid by an excess of sodium acetate, was found to dye wool and silk a beautiful orange-yellow. This yellow dyestuff, which for convenience may be called lignone yellow, is of peculiar interest as a product to be recovered that may be valuable, and it was therefore carefully studied.

## LIGNONE YELLOW.

Difficulty was at first experienced in separating the dye from the liquid. Cloth could be dyed directly in the liquid with excellent results, but on evaporation the dye lost a great deal of its coloring power. By evaporating it in partial vacuum to a thick sirup and then reducing it to dryness in a warmed vacuum desiccator, it was finally possible to obtain the desired material in dry form. It is a light-yellow powder, very porous, and extremely hygroscopic, which latter property considerably diminishes its commercial value.

Samples of woolen cloth dyed in baths prepared from the dried material in the proportion of 2 per cent of the dye, by weight, were very beautifully colored. The color is retained on boiling for half an hour in soap solution, dilute acetic acid, or dilute alkali. It withstands the action of bleaching powder, chromate, and other oxidizing agents. It will stand direct summer sunlight for two days without apparent discoloration, but it is affected on the third day; so it is, therefore, only moderately fast to sunlight.

Lignone yellow is exceedingly soluble in water and in ethyl alcohol. On evaporation of these solutions it yields a pasty mass which is completely dried with difficulty. When dried at 100° C., it is decomposed with evolution of nitrous oxide. It can be eventually oxidized with nitric acid to oxalic acid. From the manner of its formation it might be thought to be a nitro-body and in its dyeing properties it resembles picric acid; but it differs from the latter and from other nitrophenols in several particulars. Picric acid, or tri-nitrophenol, crystallizes from hot water and is difficultly soluble in cold water. The same is true of para-nitrophenol. Ortho- and meta-nitrophenols melt at 45° C. and 96° C., respectively. The three dinitrophenols are converted to picric acid on further nitration. If lignone yellow is an aromatic nitro-body, it must be more complex than any of the nitrophenols. Repeated attempts to reduce this dye were made, but no amido-body could be detected after attempted reduction with zinc dust, zinc and hydrochloric acid, iron and sulphuric acid, ammonium sulphide, hydrogen sulphide, or the electric current. In no case did nitrous acid bring about any reaction after these attempts at reduction. Generally, the yellow color was not destroyed. Neither weak chromic acid nor bleaching powder destroy the color. Long-continued boiling of the original sulphite liquor with sodium nitrite gives a liquor with feeble dyeing properties, the color being like that of the nitrated substance. It is possible, therefore, that the dye is a nitroso-compound of some complex radicle rather than a nitro-body. All attempts to prove this point resulted negatively and the question of the fundamental character of the dye remains open.

## REACTIONS OF THE AMINE CONDENSATION PRODUCTS WITH NITRIC ACID.

It was thought that the nitration of the substances produced by the condensation of the "lignone" substance with various amines might give rise to dyes of different character, and that the latter might have technical value as well as furnish some clue to the nature of lignone yellow. Accordingly, the different condensations described under "Reactions with aromatic amines" (p. 30) were submitted to the action of dilute nitric acid and the dyeing properties of the resulting solutions were tested on samples of wool. To obtain comparative results, the same quantities of the various components were used each time. As many of the amines are themselves capable of easy nitration under suitable conditions, a blank test was made each time, the amine tested being used without any sulphite liquor. The results of such blank tests as gave a dye in any way similar to that resulting from the condensation product are not recorded as positive. In each test approximately one part of the amine and one part of nitric acid were used with twenty parts of the sulphite liquor. The results of the tests are summarized in the following table:

*Nitration of products resulting from the condensation of "lignone" and amines; wool dyed in resulting liquors.*

| Amine. | Color of dye produced. | Intensity of color. | Color of blank. |
|---|---|---|---|
| Aniline | Golden yellow | Strong | Colorless. |
| Dimethyl aniline | Dark yellow | Strong | Yellow. |
| Ethyl aniline | Olive green | Strong | Olive brown. |
| Diethyl aniline | Greenish yellow | Weak | Colorless. |
| Methyl diphenylamine | Lemon yellow | Weak | Brown. |
| *m*-Chloraniline | Red, washing out yellow | Weak | Pale pink. |
| *p*-Chloraniline | Reddish orange | Strong | Colorless. |
| Dichloraniline | Reddish brown | Strong | Pale orange. |
| *o*-Nitraniline | Golden orange | Strong | Colorless. |
| *m*-Nitraniline | Golden orange | Strong | Colorless. |
| *p*-Nitraniline | Dark orange | Strong | Colorless. |
| Dinitraniline | Canary yellow | Weak | Colorless. |
| *o*-Toluidine | Golden yellow | Strong | Colorless. |
| *p*-Toluidine | Dark orange | Strong | Colorless. |
| Dibrom-*o*-toluidine | Golden orange | Strong | Colorless. |
| *o*-Tolidine | Brownish yellow | Strong | Purple. |

With the exception of one or two doubtful cases, it appears that the condensation products enter into reaction with nitric acid just as "lignone" alone does, and that the shade and intensity of the dyes produced by the reaction vary from green through orange and yellow to brown, depending on the nature of the amine that is used. Some general observations can also be made from this study. Substitution in the amido group of ethyl aniline, etc., gives greenish shades, and the lighter the substituting groups the more pronounced the green. In mono-substituted aniline, the para-compounds give the most brilliant and powerful dyes, and then in decreasing brilliancy the meta- and the ortho-compounds. The most powerful and brilliant dyes of the series in the table were those produced by *p*-chloraniline, *p*-nitraniline, and *p*-toluidine. Chlor-compounds give the most brilliant dyes; the nitro-compounds give dyes of more strength and body. As with the nitrated "lignone" alone, here also every attempt failed to produce amines from their nitrated substances. Many of the products, it is true, gave a reaction with nitrous acid after reduction, but in all such cases the reaction was that of the amine originally used and the resulting substances could be prepared equally well without the addition of "lignone." Reduction of the nitraniline products was not attempted, as too great complication would arise from the presence of the nitro-groups known to be present.

## SULPHUR DYES.

Many organic substances yield dyes when fused with a mixture of sulphur and sodium sulphide. These so-called sulphur dyes are now manufactured in a variety of colors. They are direct cotton dyes—that is, they dye cotton without the aid of a mordant—and they are very fast. Their cheapness and valuable properties have caused them to come into wide use. An attempt was made to prepare dyes of this kind from sulphite waste liquor and from several of its condensation products. In particular, it was hoped to obtain dyes of bright color, red or blue, because such colors are especially desirable and bring good prices on the market. Brown and black are much more readily made, and are consequently cheaper. Mixtures of one part dry crude "lignone" and one-half part each of sodium sulphide and sulphur were fused for fifteen minutes at a low heat. The resulting mass was extracted in hot water and the extract filtered and evaporated. From 25 grams of dry "lignone" there were made 20 grams of a green powder, soluble in water containing a little sodium sulphide. This powder was found to be a true sulphur dye, coloring cotton a dark green, which changed to a good black on oxidation in the air or on subsequent treatment in a chrome bath. Compared with commercial dyes in the market, this dye is worth about 7 cents a pound in its impure condition. About half its weight is inert material, which can be removed by proper treatment. Similar experiments in preparing sulphur dyes were made with the condensation products previously mentioned. (See p. 33.) The shades of the resulting dyes were somewhat modified by the presence of the amine, but they were all browns, grays, or black. No advantage was apparent in the use of the condensed products over that of the untreated "lignone."

## COMMERCIAL POSSIBILITIES OF LIGNONE DYES.

Two of the best dyes, namely, those resulting from the nitration of "lignone" alone and of "lignone" condensed with *p*-chloraniline, were prepared in large quantity, in order to determine the yield and the cost of the process. One hundred grams of dry crude "lignone" were treated with 50 cubic centimeters of concentrated nitric acid (specific gravity 1.42), and the resulting solution evaporated in vacuo. Seventy grams of lignone yellow were obtained. Compared with mandarin yellow, the technical dye approaching it most nearly in color and fastness, it is worth 18 cents a pound. The cost of nitric acid would be 5 cents a pound of dye. To neglect for the moment the cost of evaporating the original liquor, the margin between the cost of the acid and the value of the dye appears to be sufficient to pay for the work of handling. This would be true at places where expediency makes it necessary to evaporate the liquor in any case, and also at places where the dye could be used in liquid form as made. The cost of evaporating the liquor, however, would undoubtedly be greater than the value of the dye. It must also be borne in mind that there is necessarily a limited market for a dye of this kind—a market too limited, in fact, to permit any general adoption of this plan of utilization, even if it were very much cheaper. A similar test of the cost, yield, and value of the dye from *p*-chloraniline gave an additional cost of 9 cents a pound of dye for aniline, making the total cost for material 14 cents a pound. While the color was much more brilliant, its red shade lowers slightly its market value, pure yellows and greenish yellows being in much greater demand for use than browns. As an additional market outlet, however, this dye may possibly help in the utilization of sulphite waste liquor. The actual results attained in this investigation are not considered so important as the fact that a new and interesting series of reactions of "lignone" have been discovered. Further development of these dyes is the work of the skilled expert in textile coloring. It is not too much to expect that such an expert, possessing full knowledge of the technique of dyeing, will be able not only to simplify and to reduce to a practical working basis the methods herein outlined, but also to discover new and more valuable products by further experimentation along similar lines.

## CONCLUSION.

The foregoing study of sulphite pulp waste liquor and of the possible utilization of the organic material in it may be summarized in a few sentences.

Stream pollution by the waste from sulphite pulp mills is extensive and wasteful; every year over two and a half billion pounds of solid matter from this source are turned into the rivers and lakes of the United States.

The problem of utilizing this immense amount of waste matter has been studied for a long time, and numerous processes for using or for destroying it have been devised, but they are all unsuccessful, either because there is only a limited market for the proposed product or because the suggested process is prohibitively costly.

Successful disposal of the sulphite waste liquor lies obviously in the utilization of the so-called "lignone" in it, but aside from the employment of this substance to a slight extent as an adhesive and as a source of tannin, no practicable way for its direct use has been devised.

The waste consists principally of wood material separated from the wood fiber by the action of a strong sulphite solution on wood chips; it is a compound of "lignone" with sulphur; but the exact nature of the union has not been definitely demonstrated.

Experimental evidence indicates that the sulphur-bearing compound in the waste liquor is not a true sulphonic acid; at all events, it does not react like an ordinary sulphonic acid. Its condensation with the aromatic amines point to its probable aldehydic nature.

Nitration of "lignone" and of its amine condensation products gives a series of dyes the shade and intensity of which vary from green through orange and yellow to brown, depending on the nature of the amine that is used. These substances dye wool directly, giving brilliant colors that are fast to soap, acids, and alkalies, and reasonably fast to sunlight. One of them, named lignone yellow, and made by nitrating crude "lignone" itself, dyes wool and silk a beautiful orange yellow. Fusion of "lignone" with sodium sulphide and crude sulphur produces a sulphur dye that colors cotton dark green, changing to black on treatment in a chrome bath.

A search for new compounds, such as that made in the present investigation, possesses the serious drawback that much time and effort may be spent without tangible results; on the other hand, an important discovery may be made at any time. Certain reactions brought to light in this work with "lignone" reveal great possibilities. Though the dye called lignone yellow has only slight commercial possibilities and is at best but a partial solution of the major problem, yet the opportunities for further progress along this line are pregnant with the ever-present chance of discovering valuable substances. The number of "lignone" condensation products is almost unlimited, and a wide field for investigation is thereby offered. Only a small portion of a large and interesting territory has been covered by these experiments and the results are by no means conclusive. But it is hoped and expected that the mere reopening of this old and practically abandoned problem by calling attention to these new lines of attack may result in renewed investigation and in the ultimate utilization of a substance that to-day is probably the most valuable waste material known to industrial chemistry.

# SURVEY PUBLICATIONS ON STREAM POLLUTION.

The following water-supply papers of the Survey discuss stream pollution. Nos. 103, 152, 185, and 194 can be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., at the prices stated. Any of the others will be sent free, while the edition lasts, on application to the Director of the United States Geological Survey.

72. Sewage pollution in the metropolitan area near New York City and its effect on inland water resources, by M. O. Leighton. 1902. 75 pp., 8 pls.
79. Normal and polluted water in northeastern United States, by M. O. Leighton. 1903. 192 pp.
103. A review of the laws forbidding pollution of inland waters in the United States, by E. B. Goodell. 1904. 120 pp. 10c. (See No. 152.)
108. Quality of water in the Susquehanna River drainage basin, by M. O. Leighton, with an introductory chapter on physiographic features, by G. B. Hollister. 1904. 76 pp., 4 pls.
113. The disposal of strawboard and oil-well wastes, by R. L. Sackett and Isaiah Bowman. 1905. 52 pp., 4 pls.
121. Preliminary report on the pollution of Lake Champlain, by M. O. Leighton. 1905. 119 pp., 13 pls.
144. The normal distribution of chlorine in the natural waters of New York and New England, by D. D. Jackson. 1905. 31 pp., 5 pls.
152. A review of the laws forbidding pollution of inland waters in the United States (second edition), by E. B. Goodell. 1905. 149 pp. 10c.
179. Prevention of stream pollution by distillery refuse, by Herman Stabler. 1906. 34 pp., 1 pl.
185. Investigations on the purification of Boston sewage, by C.-E. A. Winslow and E. B. Phelps. 1906. 163 pp. 25c.
186. Stream pollution by acid-iron wastes, a report based on investigations made at Shelby, Ohio, by Herman Stabler. 1906. 36 pp., 1 pl.
189. The prevention of stream pollution by strawboard waste, by Earle B. Phelps. 1906. 29 pp., 2 pls.
192. The Potomac River basin—geographic history; rainfall and stream flow; pollution, typhoid fever, and character of water; relation of soils and forest cover to quality and quantity of surface water; effect of industrial wastes on fishes; by Bailey Willis, R. H. Bolster, H. N. Parker, W. W. Ashe, and M. C. Marsh. 1907. 364 pp., 10 pls.
193. The quality of surface waters in Minnesota, by R. B. Dole and F. F. Wesbrook. 1907. 171 pp., 7 pls.
194. Pollution of Illinois and Mississippi rivers by Chicago sewage; a digest of testimony in the case of the State of Missouri *v.* the State of Illinois and the Sanitary District of Chicago, by M. O. Leighton. 1907. 369 pp., 2 pls. 40c.

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