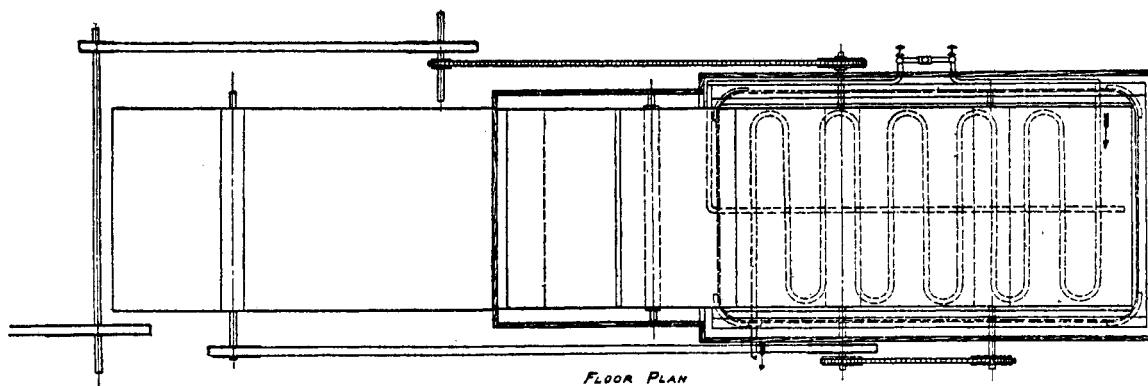


paste with sodium formaldehyde sulfoxylate. This rendered the discharge more energetic and also hindered the reoxidation, but it was necessary to handle the material very quickly to avoid tarnishing the whites. The usual conditions of the printing rooms rendered the production of uniform results almost impossible and little practical use was made of the process in this country.

However, in the last two years a notable advance has been made owing to the discovery that certain bases of the substituted ammonium type would combine with indigo white to form stable compounds which

higher cost the commercial product now represents the standard of indigo prints. The gain to consumers is in the same proportion: for the strength of the material is not affected and after the garments are washed three times the whites are no longer holes but remain the original material.

The zinc-formaldehyde-hydrosulphites are used solely for removing the dyestuff and colors from previously dyed material and have little interest for the phase of the subject under consideration. Their great advantage lies in the fact that the strength of the fiber is not affected.



do not oxidize in the air. Further experiments proved that this property was characteristic of compounds of certain tertiary bases with benzyl chloride, its homologues and analogous bodies and their substitution products. In the presence of zinc oxide desirable reddish to yellow shades can be obtained by this method.

But in order to obtain white discharges the compounds obtained in the discharge process had to be made readily soluble. It was found that this could be done by the substitution of a sulphonic group in the benzyl nucleus. The yellow compound obtained by using a substance of this nature in the formaldehyde sulfoxylate discharge paste is readily soluble in alkalis and being easily removed from the material leaves the patterns clear.

Thus the problem of satisfactory indigo discharges was solved. For certain considerations the discharge material is not sold as such but in combination with sodium formaldehyde sulfoxylate as hydrosulphite C L or rongalite C L, according to the maker.

The practical method of handling is simple. The discharge pastes are made up with 20 per cent. of the sulfoxylate discharge compound, 8 per cent. zinc oxide, 4 per cent. anthraquinone, 30 per cent. paste, with suitable thickening. The material is printed, dried, steamed in the before described steamer for 3-5 minutes at 100°-103° C., washed in hot water, then passed through an alkaline bath, washed and dried. In this process, the pastes are perfectly stable and after printing and steaming the material can be left indefinitely before clearing. The writer kept a piece for two months before clearing and the resulting whites were perfect.

The process has been adopted by the largest indigo printers in this country. In spite of the fact of the

The increase in the use of hydrosulphites and the formaldehyde compounds has been most marked and the probable consumption in the textile industry in the United States for the year 1911 was not far from one million pounds.

NEW YORK CITY.

THE EFFECT OF "LIME-SULPHUR" SPRAY MANUFACTURE ON THE EYESIGHT.¹

By JAMES R. WITHROW.

About two years ago, the writer was called upon to take charge of the installing of a "Lime-sulphur" department for a manufacturer engaged in other lines of chemical manufacturing. Preliminary to starting industrial experimentation, a very thorough laboratory study had been carried out by the manufacturer's regular chemist. This work reviewed in a most capable manner about all the recommendations of recent chemical and experiment station literature concerning "lime-sulphur" preparation. As a result of this work a formula was evolved, which was used as a basis for manufacturing experiments. The laboratory experiments themselves were never made in larger than five-gallon apparatus. The writer witnessed, from time to time, these experiments or portions of them and at no time noticed anything causing discomfort. The laboratory assistant, who did most of the experimental work for the company's chemist and was constantly in contact with the material and its fumes, never noticed any effect or discomfort at any stage of the laboratory work, which extended through several months. To be sure, there was the ever present odor of hydrogen sulphide or at least a similar odor. This was never offensively strong. At no time was it

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

so noticeable as to compel enforced ventilation.

The writer's business was to accept the work as completed in the laboratory and transfer it to factory operation. The first factory experimental runs were made on about a 12-barrel scale. These experimental cooks were made to get factory scale data for construction work and also to uncover any unforeseen operation difficulties. The product had varying specific gravity from 45° to 32° Bé., depending on the purpose of the experiment. The final solution of calcium polysulphide or so-called "lime-sulphur" contained about 25 per cent. sulphur and about the equivalent of 10 per cent. calcium oxide, when the specific gravity was about 33° Bé. Twelve barrels of this product therefore would contain 1625 pounds of sulphur and the equivalent of 650 pounds of lime.

The first few cooks aroused no comment from employees about the building, which was a large one of four stories, beyond what would come from persons unaccustomed to hydrogen sulphide. In the course of the next week or two, however, the weather had become quite cold and the normal ventilation by means of the windows was much diminished. Again no particular effect was noticed at first. The "cook" digester was a steam jacketed cylindrical tank roughly 5' X 5' and supplied with a cover and a small ventilating pipe. This pipe was inadequate for proper ventilation of tank and would have been useless anyway, for the top of the "cook" tank was usually open during the experimental runs for observation purposes. The man in charge of the cooks usually stationed himself at the opening to become familiar with boiling conditions within the tank during the various runs under different conditions.

Within a cook or two, after the windows were closed to diminish the cold conditions, the man in charge of the cook became aware of a smarting sensation in and around the eyes. The eyelids became red. The writer was constantly about the tank, but was only occasionally at the tank opening and felt little or no discomfort, though there was a slight burning feeling about the eyes. The room became partially filled with condensed steam at times and finally about 8.00 P.M., during a slightly prolonged run, the writer noticed that the amount of vapor in the room was greater than usual and that the incandescent electric lights had a halo of some eighteen inches in diameter when viewed through the fog; the halo tended to have rainbow colors. An hour or two afterwards, the writer found the same conditions as to fog and halo to exist in his room in his hotel and concluded that his eyesight was affected. Cold water was applied liberally and he turned into bed and went to sleep at once. In the morning the blurred eyesight was about as bad as the evening before. The foreman, who stood at the opening of the cook tank, had gone home at the end of the run at the time the writer did. He was unable to report for work next day. His eyes were much inflamed and were too sensitive to light to open them. He said they pained and felt gritty under the eyelids. He was back at work again in a couple of days. In the case of the writer, with the liberal use of saturated

boric acid solution, the blurred vision gradually returned to normal during the course of a week's absence from the manufacturing operation. There was a recurrence of the blurred effect at another time, which rendered vision almost impossible, but it rapidly wore off and at no time was there any pain. The foreman never again had an attack after his initial experience. None of the workmen were affected after proper precautions were taken.

At one time however, when a batch was being concentrated by boiling down, the cover was thrown open to expedite evaporation. In the same room some distance away, two workmen were barreling off finished product. Both the foreman and myself were actively engaged about the cook tank and were practically unaffected. Of the two workmen mentioned however, the thin one was very much affected and said he suffered agony all night and next day, while the corpulent one was entirely unaffected. Other workmen were in and out during the cook but none were affected. The one of the two mentioned above as unaffected has, since starting regular operation in the new plant and in fact during the rest of the experimental runs, been in active charge of the "cooks" and has never become affected, beyond possibly a slight reddening of the eyes.

No one at all has been affected in anyway since the new plant was installed with its ample facilities for ventilation. Inquiry directed to other manufacturers disclosed similar experiences. One manufacturer's experience was so bad that he at once knocked one side out of his cooking room. This is undoubtedly effective, but from the writer's experience unnecessary. All that is required is a hood over the cook tank, which will carry all vapors out doors, and a "cook" room which is high ceilinged and reasonably well ventilated. Providentially the copious evolution of steam has caused most plants to provide hood-covered tanks, thus avoiding the unexpected trouble we are discussing.

A search of the literature of "lime-sulfur" available to the writer found no mention of the effect of the eyes. The suggested reactions to explain the action of sulfur on calcium hydroxide and water, varied as they were, gave no clue to what might have been the body which gave rise to the trouble. During a subsequent study of polysulfide literature in general, however, it was found that Bloch and his pupils¹ had prepared polysulfides of hydrogen of the formulas H_2S_3 and H_2S_4 . The latter is formed by heating the former and is easily volatile. The fumes of these polysulfides are said to have a penetrating disagreeable odor and their vapors attack the mucous membranes. Thorpe says their vapors attack the eyes.² They are decomposed by alkalies and therefore would not exist very long in the lime-sulfur cook, but if they were being given off in mere traces, continuous exposure to such fumes would naturally cause discomfort.

Hydrogen sulfide itself, however, may have been the cause of the trouble. It has been shown to be a

¹ *Ber. d. chem. Ges.*, **41**, 1961; *Am. Chem. J.*, **41**, 155.

² *Dict. Applied Chem.*, **3**, 699 (1893).

product of the evaporation of a solution of calcium polysulfides.¹ Hydrogen sulfide could not likely have been the cause, unless the symptoms of H₂S poisoning recorded are the effects of only sudden or brief exposure to large amounts of the gas and that prolonged exposure to dilute H₂S would cause a different series of violent symptoms. This latter assumption does not appear probable for in such cases where H₂S was permitted in the atmosphere of laboratories in small amounts, the usual symptoms, only not so pronounced, were the result. The only recorded symptom of hydrogen sulfide poisoning observed in the cases under discussion was the occasional occurrence of headache. This was to be expected, since hydrogen sulfide was itself being evolved to some extent.

It should be mentioned, however, that K. B. Lehmann² mentions cases where "intense irritation of eyes, nose and throat" occurred within five to eight minutes of exposure to a concentration of 0.3 per thousand of hydrogen sulfide, but no affection of the sight is mentioned even in this extreme case. In long exposure to lower concentrations, such as would correspond with the case of hours of exposure in lime-sulfur cooking, the action recorded is on the respiratory tract. These symptoms appeared entirely absent in the lime-sulfur cases as also were all the other common symptoms (except headache), such as muscular weakness, etc. A tendency to conjunctivitis, a symptom of chronic hydrogen sulfide poisoning, may have been present in the case of the man in charge of the cooks. He was the man, however, whose eyesight itself was never affected. The writer has suffered at other times in the last six years, most of the symptoms of slow hydrogen-sulfide poisoning, due to inadequately ventilated, over-crowded and poorly arranged university laboratories, but the symptoms in the lime-sulfur experience were quite different. In fact the usual muscular weakness and general depression as caused by hydrogen sulfide were not experienced at all in the lime-sulfur manufacture. It should be mentioned also, that the writer has been informed that attendants at "sulphur" baths have had their eyesight temporarily affected in a similar fashion. Volatile polysulphides may be present in this case also, although they have not been proven to the writer's knowledge to be present in either case. This would be an interesting point for some favorably situated person to develop.

It seemed possible therefore that these hydrogen polysulphides might have been the cause of the action on the eyesight of the vapors from the boiling of a mixture of sulphur, lime and water.

It may be stated at this point that this indication of the presence of hydrogen polysulphide in the vapors of the lime-sulphur cooks might have an influence upon the solution of the problem of the actual reactions involved in lime-sulphur preparations, a mooted question at the present time. The trouble with the eyesight always came when a batch was being concentrated by evaporation before filtration and not during ordinary cooks.

¹ Divers, *J. Chem. Soc.*, **1884**, p. 284.

² Arch. F. Hygiene, Bd. XIV, 1892, 135; Blyth, "Poisons, Their Effects and Detection," 3rd. Ed., C. Griffin and Co., London, p. 73.

It seemed worth while to record these facts as a warning, at least, as to the serious dangers of lime-sulphur manufacture in the absence of adequate ventilation. This is all the more necessary since it is probable that attention has not already been frequently called to the matter, because ordinary ventilation precautions only, are necessary to avoid all trouble, and therefore the average manufacturer has not had the experience or it has appeared so seldom that the isolated affections of a workman now and again may have been attributed to something else. It is worth noting also because the mere occurrence of a cold spell of weather gave the opportunity of experiencing this difficulty possible in lime-sulphur manufacture, so that otherwise it might never have occurred at this plant or only in such isolated cases as to destroy any connection between cause and effect.

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PHENOL-FORMALDEHYDE CONDENSATION PRODUCTS.¹

By L. H. BAEKELAND.

The resinous or amorphous products resulting from the action of phenolic bodies upon formaldehyde have lately attracted considerable attention on account of their rapidly increasing applications for industrial purposes.²

It is questionable whether this general designation of "condensation products of phenols and formaldehyde" should be maintained much longer. Indeed, it is well known that these products can be obtained without the use of so-called formaldehyde. In fact, the first condensation products thus described were produced without the use of formaldehyde,³ and it is generally accepted that other methylene compounds, for instance, methylal, trioxymethylen, hexamethylenetetramin, etc., can replace formaldehyde in this reaction. The fact that hexamethylenetetramin can suitably replace formaldehyde in the formation of the infusible phenolic condensation products was published as far back as December 31, 1907, by Lebach.⁴

Lately, I have succeeded in producing fusible resinous condensation products identical with those described by Blumer, DeLaire, etc.,⁵ by introducing a mixture of salicylic acid and an inorganic acid in the cathode compartment of an electrolytic cell in which sodium chloride is electrolyzed, a mercury cathode being used. According to the well known reaction of Kolbe, the carboxyl group of salicylic acid is introduced by reacting with CO₂ on phenolate of sodium, so that we have here an example of the possibility of introducing indirectly the methylene group as CO₂, then reducing the carboxyl group by means of nascent hydrogen. A similar observation

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² Baekeland, *THIS JOURNAL*, **1**, No. 3, 149 (1909); No. 8, 545 (1909); **3**, No. 12, 932 (1911).

³ *Ber.*, **5**, 1905; **19**, 2009, 3004; **25**, 3477; **27**, 2411.

⁴ Knoll patent, Belgium, No. 204,811, December 31, 1907. Ditto. Wetter (Knoll) British patent, No. 28,009, 1907, owned by the Bakelite Gesellschaft of Berlin.

⁵ Baekeland, *THIS JOURNAL*, **1**, 545 (1909).