the bullet and placing it on the scale; on balancing, the percentage of tin or antimony is read off directly on the beam. The balance is delicate enough to rise or fall with a movement of less than one-half of one per cent., while, with care, duplicate bullets may be cast not varying in weight over one-half per cent. The only precautions to observe are to continue the pouring until the bullet is set, in order to avoid a shrinkage cavity, and not to pour into a hot mould, which would necessarily be larger and cast a heavier bullet. The whole operation of melting, casting, and weighing can be performed easily in three to five minutes, and, if need be, by any workman of ordinary intelligence.

Nearly a score of these outfits have been sold by Mr. Richards during the last six months, and their introduction into the industries using these alloys has displaced the rule-of-thumb practice by accurate calculation, and brought many a dishonest manufacturer to his proper deserts.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.[1]

BY WALTER D. FIELD.

PART III.

(Continued from p. 498.)

THE peculiar form in which pyroxylin is deposited from its ether-alcohol solution, first called the attention of experimenters to it as a means for producing improvements in the various industrial arts. Photography was the first of the industrial arts to utilize this peculiar property of soluble nitrocellulose.

Later English experimenters made attempts to use pyroxylin as the base for an imitation bone, ivory or hard rubber. Parks, Spill, Greening, and others labored industriously to find some way or some solvent that would dissolve pyroxylin so they could obtain it in solid blocks suitable for turning and molding.

Four years after Scott Archer used pyroxylin in photography, Parks filed his first patent for the use of a solution of pyroxylin. (Eng. Pat. No. 2359, Oct. 22, 1855.) Then again in May, 1858 (Eng. Pat. No. 1090), John MacIntosh proposed the use of pyroxylin dissolved in a solvent composed "of equal parts of wood spirit and coal naphtha" for use in the insulation of wire. In 1864 Parks (Eng. Pat. No. 2675) proposed the use of pyroxy-

[1] Read before the World's Congress of Chemists, June, 1893.

lin with gum ballata and says: "I employ as a solvent which I prepared by distilling wood naphtha with calcium chloride." Parks seems to recognize the desirability of using a solvent as near anhydrous as possible, and says the greater the quantity of calcium chloride used the stronger the solvent. But because of his solvent Parks was unable to make his experiments successful, and so he begins to search for solvents that would not evaporate so quickly and would enable him to work the pyroxylin solution in heated rolls. Parks finds that nitrobenzene, aniline, glacial acetic acid, and camphor dissolved in the more volatile solvents, methyl alcohol and alcohol-ether are much better for use in producing a plastic as they are less volatile and develop greater solvent action under the influence of heat.

Spill (Eng. Pat. No. 3102, 1869) finds camphor in alcoholic solution, camphor oil, aldehyde alone or with alcohol, solvents of pyroxylin. Ethyl and methyl acetates were found to be solvents of pyroxylin by Pelouse (*Compt. rend.*, **24**, 2), and ether-alcohol by Dominte and Merard (*Compt. rend.*, **29**, 390). Acetone was known to be a solvent of pyroxylin prior to 1864. To the solvents already given none were added until 1882, when John H. Stevens took out a series of patents, in which he gives a large number of new solvents for use in the production of solid compounds of pyroxylin. In these patents (U. S. P. Nos. 269,340, 269,341, 269,342, 269,344, 269,345,) he names the following substances: methyl nitrate, ethyl butyrate, ethyl valerate, ethyl benzoate, ethyl formate, methyl salicylate, amyl formate, amyl acetate, amyl butyrate, amyl valerate, ethyl sebacylate, ethyl oxalate, diamyl oxide, which are all active solvents of pyroxylin, that is they are solvents at the usual temperatures. He names dinitrobenzene and coumarin as latent solvents, that is, they are solvents at their melting points or when dissolved in alcohol. Stevens also finds acetal, amyl nitrate, and amyl nitrite in alcoholic solution to be solvents of pyroxylin at ordinary temperatures.

In 1889 Robert Shupphous took out a series of patents (U. S. P. Nos. 410,204, 410,205, 410,206, 410,207, 410,208, and 410,209). He finds propyl and isobutyl alcohols with camphor active solvents, and the ketones, palmitone, and stearone in alcoholic solution, also alpha and beta naphthol with alcohol, and anthraquinone (diphenylene diketone) in alcoholic solution. Iso-valeric aldehyde and its derivatives, amyliden-dimethyl and amyliden-diethyl ethers, Shupphous finds are active solvents of pyroxylin.

In 1892 August Sayer (U. S. P. No. 470,451) informs us that diethylketone, dibutylketone, dipentylketone, and the mixed ketones, methylethyl, methylpropyl, methylbutyl, methylamyl, and ethylbutylketones are active solvents of pyroxylin. Still later Leonard Paget (U. S. P. No. 494,793) finds that methylamyl oxide is a solvent but ethylamyl oxide (U. S, P. No. 494, 792) is not a solvent.

The solvents of pyroxylin can be divided into the following general classes: First, those which are solvents, without the aid of heat or solution in alcohol; second, those that are solvents when dissolved in alcohol. These solvents are those which also develop a solvent action when heated to their melting point in combination with pyroxylin.

We also find that chemically the solvents of pyroxylin can be grouped into classes as follows: Two of the monohydric alcohols; compound ethers of the fatty acids with monohydric alcohols; aldehydes; simple and mixed ketones of the fatty acid series. These classes include the greater number of the solvents of pyroxylin those not included are as follows: Amyl nitrate and nitrite, methylenedimethyl ether, ethidenediethyl ether, amyl chloracetate, nitrobenzene and dinitrobenzene, coumarin, camphor, glacial acetic acid, and mono, di, and triacetin.

Another division of the solvents of pyroxylin is necessary when we consider their properties. We find it necessary to divide the solvents of pyroxylin into two great classes according as they are hygroscopic or non-hygroscopic. To the first class belong acetone, methyl acetate, ethyl acetate, methyl alcohol, aldehyde, ethyl formate, propyl formate and acetate. These solvents when they deposit pyroxylin from their solution, also absorb water and this precipitates the pyroxylin in the form of a white cloud on the surface of the deposited film. In some cases this cloudiness extends entirely through the film and it is like chalk dust in appearance.

Dr. Guido Wolfram (*Dingler's Poly. J.*, **230**, 156,) says: "Pentanitrocellulose is soluble in acetone, acetic ether, and still easier in a mixture of the same with ethyl ether. The solution gives a cloudy layer (matte) or film on evaporation." The pentanitrocellulose was not the cause of the cloudy film. for if he had used anhydrous solvents and evaporated his solution in a chamber free from moisture he would have obtained clear films.

Wolfram says: "The solution of the tetranitrocellulose in acetic ether, acetone, and wood-spirit, wood-spirit ether, acetic ether, ether, and acetone ether, gave a hazy opaque layer—a proof that the obtaining of a vitreous layer depends not only on the substance but likewise on the kind of solvent used." If Wolfram had used alcohol instead of ether in combination with the hygroscopic solvents he would have obtained clear transparent or glassy films on the evaporation of the solvent by reason of the alcohol absorbing the water and preventing the precipitation of the pyroxylin.

All the non-hygroscopic active solvents of pyroxylin deposit it from solution as a transparent, glassy film.

The action of the various solvents towards pyroxylin is often very peculiar. Thus is the case of the alcohol-ether solvent, neither the ether nor the alcohol is a solvent yet when combined they produce an active solvent. Camphor when dissolved in alcohol produces a good solvent; on the other hand camphor dissolved in the ketones reduces their solvent action. Nitrobenzene gives a solution that is granular, it seems to merely convert the pyroxylin and not to dissolve it, on the addition of alcohol (distilled from lime) we have at once a solution, that is, the granular appearance disappears and the solution becomes homogeneous.

The acid mixture and the method of nitrating has much to do with the action of the various solvents. The influence of water (uncombined) in the acid mixture, the influence of the immersion temperature, and the effect of increasing the nitric acid and diminishing the sulphuric acid, all influence the solubility of the resulting product.

We will consider first the influence of mechanically mixed water on the solubility of the pyroxylin.

Starting with a mixture of eight pounds of nitric acid, sp. gr. 1.435, and sixteen pounds of sulphuric acid, sp. gr. 1.83, and one-twentieth part by weight of cotton, first add six ounces of water and immerse the cotton at 60° C. The cotton is finished in ten or twelve minutes, and when washed and dried is found to be very pulverulent, or rotten and dusty, and occupies a much smaller bulk than the non-pulverulent variety insoluble in methyl alcohol. This pyroxylin is very soluble in methyl alcohol and in all hygroscopic solvents, giving with them limpid thin solutions.

Again taking the same proportions of acids of the gravities as given above, and the same amount of cotton for nitration, and adding nine ounces of water, the temperature of the immersion this time being 65° C., we find the pyroxylin produced very much more soluble in methyl alcohol than that produced by the first formula. Also that all its solutions are more limpid or fluid.

In this formula we have the following amounts of water: Eight pounds nitric acid, sp. gr. 1.435, contains 2 pounds, $2\frac{2}{5}$ ounces water. Sixteen pounds sulphuric acid, sp. gr., 1.83, contains 1 pound, $1\frac{23}{25}$ ounces water. Nine ounces water added makes the total water in the acid mixture 3 pounds, $13\frac{8}{25}$ ounces.

Now if we took a weaker nitric acid that would contain the desired water, without addition, as in the following formula: Eight pounds nitric acid, sp. gr. 1.40, contains 2 pounds, $10\frac{4}{5}$ ounces. Sixteen pounds sulphuric acid, sp. gr. 1.83, contains 1 pound, $1\frac{23}{25}$ ounces. Giving a total of 3 pounds $12\frac{8}{25}$ ounces. We would naturally suppose that this formula, containing as it does within an ounce of the same amount of water as the first formula, would produce pyroxylin having almost identical solubilities with that produced by the first formula. The two formulas do not, however, produce pyroxylins having the same solubilities, using, of course, in nitrating, the same temperature.

The pyroxylin produced by the formula containing the mechanically added water, is very soluble in methyl alcohol and hygroscopic solvents, but only imperfectly soluble in non-hygroscopic solvents, for instance, the compound ethers. Whereas the pyroxylin produced by the second formula, containing no mechanically added water, is perfectly soluble in the non-hygroscopic solvents, and its solutions in the hygroscopic solvents are inclined to be heavy. The nitric acid used in these experiments was water-white and free from any dissolved nitrogen oxides.

The pyroxylin made from the formula containing the mechanically added water yields a film that is very contractile, that is, when it is deposited from its solution on a piece of plate glass it differs from other pyroxylins in drying to a much smaller bulk.

It was, however, the fact that the non-hygroscopic solvents of pyroxylin would deposit it as a film having great strength and transparency that led to its use for producing a varnish which could be applied to brass and silverware by simply dipping articles in it. The person who practically applied these properties was Richard Hale (U. S. P., No. 471,422). Hale uses the following solvent: Amyl acetate, four volumes; petroleum naphtha, four volumes; methyl alcohol, two volumes; pyroxylin, four to five ounces to the gallon of solvent. In this case, Hale has used petroleum naphtha to hasten the drying qualities of the varnish, so that it would set on the article to be varnished before it had a chance to run off. It was, however, the non-hygroscopic character of the solvent that made the varnish successful when it came to practical application. This very formula, or one which is a very slight modification, is used to-day in the production of thousands of gallons of pyroxylin varnish.

The varnish made on this principle is also used for varnishing pens and pencils and it gives them such a superior finish that they command a higher price than those varnished with the ordinary varnish.

And now the last industry that has sprung up, because of the wonderful properties of pyroxylin when deposited from its solution in a non-hygroscopic solvent, is the production of photographic films, flexible glass we would call it, and really, what better name could we give it? Henry Reichenbach made the first application of the use of a solvent of pyroxylin, that was practically non-hygroscopic, to the production of a photographic film. In his patent, issued in December, 1889, Reichenbach gives a formula, but as this formula is no longer in use, from the fact of its being too largely composed of hygroscopic solvents, there is no need of producing it here. It has been due to the recognition by experimenters, that by a suitable combination of solvents solutions could be produced that would flow fast or slow, set rapidly or slowly, and produce the varied products desired, that the industry has developed so rapidly.

Hyatt's discovery that a mixture of camphor and pyroxylin when heated could be worked like rubber was the beginning of the success of the celluloid industry. Hyatt discovered the latent solvent action of camphor.

RECENT WORK ON THE SUGARS.

BY B. B. ROSS.

Received May 14, 1894.

THE ESTIMATION OF INVERT SUGARS.

Bauman (*Ztschr. des Ver. f Rubenzucker Ind.*, **42**, 824) gives a new table, based upon the original table of Herzfeld, for the calculation of invert sugar percentages in solutions containing considerable proportions of sucrose. The table is quite similar to that of Herzfeld, but provides for the employment of only five grams of material instead of ten grams, as in the old table.

Ehrmann (*Bull. Assoc. Chim., France*, **10**, 537) describes a method for the indirect gravimetric estimation of glucose by means of the reduction of one of the double platinum chlorides by the copper suboxide thrown down by the invert sugar.

The suboxide, precipitated in the usual manner is brought upon the filter and washed thoroughly; the reduction of the precipitate is next effected by pouring upon the filter a small amount of a concentrated solution of potassium platino or sodium platinochloride, the red precipitate of suboxide being superseded by a black deposit of platinum.

After washing and igniting the residue, the amount of invert sugar corresponding to the weight of platinum obtained, can be readily calculated.

The author claims that this method is more rapid and easy of execution than the reduction of cuprous oxide in a current of hydrogen, and that it is also more exact, for the reason that the atomic weight of platinum is much higher than that of copper.

Nihoul (*Chem. Ztg.*, **17**, 500) refers to the gravimetric