according to Clifford Richardson* and others, these hydrocarbons are probably polymethylenes. From a large number of combustion determinations made with bitumens, it may be safely stated that many of the bitumens are probably polymethylenes of various series, as above. There are, of course, substances in bitumens such as sulphur and nitrogen, which probably exert very little influence on the material from an actinic point of view. Assuming, therefore, that the hydrocarbons are of the character described, we should have under the combined action of the oxygen of the air and the actinic rays of the light, sometimes, in conjunction with moisture, a favourable condition where oxygen would combine with hydrogen, and carbon be set free. Therefore, if this reaction takes place, all bitumens in a short time ought to become carbonised and deposit relatively pure carbon on their surfaces, and this is exactly what takes place, the action of the sunlight probably resulting in a combination of the hydrogen with oxygen, and a deposit of what appears to be carbon takes place. If this, then, is the first lucid explanation of the decomposition of bitumens in sunlight, it is the explanation of the cause of the valuelessness of pure bitumens as protective paints for exterior purposes. Even the addition of a small amount of bitumen to a large percentage of otherwise good paint will result in the decomposition of this paint when exposed to the direct action of moisture and light.

We have no such action when materials are used which are glycerides of fatty acids, such as fish oil, Chinese wood oil, and linseed oil. Indeed, any one of these three oils are lightproof in a very large degree, and fish oil and Chinese wood oil are both heat proof and light proof. Linseed oil, however, unless prepared with fossil resins, is not waterproof, but fish oil is more waterproof, and Chinese wood oil most waterproof of all. At the same time, pure Chinese wood oil is less lightproof, next comes fish oil, while linseed oil is most lightproof, and there would appear to be an established ratio that a paint or varnish containing the least amount of oxygen is the least lightproof and the most waterproof, and the paint containing the largest amount of oxygen is most proof against light, and least waterproof.†

In conclusion, and as evidence of the correctness of these statements, if a sheet of metal or wood be painted with asphaltum or bitumen-paint and exposed to sunlight and air, the coating will be rapidly decomposed, and after a lapse of 20 days, probably carbon will be set free. At least, this is a deduction from the nature of the bitumens. Minute scrapings from the surface of exposed bitumens show that the principal constituent is carbon, and whereas the original material contains much less, the exposed bitumen shows over 95 per cent. of carbon, the remainder being principally hydrogen, with a small difference, which is evidently oxygen. This shows that the general reaction tends to produce carbon. The painting of concrete to preserve it against the action of moisture and frost is destined to become as large an industry as the painting of wood, and those who have tried asphaltum paints for this purpose have already found to their sorrow that disintegration takes place in a very short time, even though the material be perfectly proof against the alkaline action of the lime in the concrete, and as linseed oil paint is rapidly destroyed by concrete itself, owing to the interaction of the lime and the linseed oil, we have to look for other materials with which we can coat concrete in order to preserve not only its appearance, but the very structure itself.

Regarding the action of sunlight on pigments, it is well known that lithopone is rapidly acted upon by light, and direct sunlight turns it a dark gray, but frequently overnight the colour leaves it and it is brilliant white again in the morning. English vermilion (mercuric sulphide) is also acted upon by sunlight, and forms first a brown compound and then a black compound of mercury. This has been regarded as mercurous sulphide or as a

sub-sulphide of mercury, but on this question the writer has doubts. Some of the oxides of iron, particularly the bright red ferric oxides, are affected by light, and a compound results which from bright red turns to brown, probably a change tending towards the formation of ferrous oxide.

We know that a large number of the organic dyestuffs tend to bleach in the sunlight, but sunlight alone is never very active regarding the decomposition of colours when air is excluded, for even mercury vermilion is regarded as permanent when it is covered by a coat of varnish. This is largely true of the organic lakes and finer colours used for coach painting. Linseed oil itself is bleached by sunlight, but this is a chemical change produced by the actinic rays in which the green chlorophyll is changed to pale yellow.

PREPARATION AND USES OF ANHYDROUS STANNIC CHLORIDE IN SILK DYEING.

BY ELMER A. SPERRY.

STANNIC chloride, discovered in 1608 by Libavius, has a sp. gr. of about 2.3, and possesses wonderful fluidity; the pure liquid is described by various authorities as a yellow liquid, but it is, in fact, colourless and very brilliant owing to its high refractive index. It is extremely hygroscopic, having greater avidity for water than sulphuric acid, yet unlike other hygroscopic substances, it seems impossible to wet it, although its avidity for moisture is evident from the high degree of heat developed upon the addition of moisture or water. As fast as the water is added, stannic chloride hydrate is formed and separates out as a solid. This separated material constitutes the "butter of tin," or oxy-muriate of tin of commerce, but has not been prepared in this manner except in the laboratory, although this solid was discovered about 160 years after the work of Libavius. This heavy fuming liquid has been looked upon in the past as of no practical value, never having been used in the arts nor even as an analytical reagent. Its price has always been extremely high, and is at present about \$100.00 per gallon.

At a comparatively recent date, a Dutch chemist discovered that cochineal was made to yield a permanent pigment of great brilliancy in the presence of a dilute stannic chloride solution. This solution was made by dissolving tin in hydrochloric acid, adding additional acid and oxidising the solution to stannic chloride. This discovery was quickly taken up by the dyeing industry, but the chloride solutions continued to be prepared as used, directly from tin as outlined above. The chlorates are usually used as oxidising agents, leaving chlorides as an impurity, which is added to the usual impurities encountered in the commercial acids employed. These solutions may be raised to a concentration of 50° and sometimes 60° B. for more economical shipping, and then again diluted by the dyer before being used. It has long been known that the mordanting and weighting of the fibre, employing tin chloride solutions, is accomplished only by the stannic chloride present therein, this being the only useful factor in the solution. It has been known for some time that to the impurities in solutions can be definitely traced tendencies to weaken the fibre and render light-sensitive the threads and fibres treated. It is also known that some of the impurities operate to bring about a gradual deterioration in the strength of the material, which is sometimes also hastened by exposure to light.

Without entering further into the discussion of this question, it will suffice to say that for all purposes of dyeing the problem is greatly simplified if only materials which are chemically pure can be employed, and the solutions freed entirely from the presence of any adulterants and deleterious or foreign bodies. The dyers' solution is active only in proportion to the amount of stannic chloride which the solution contains; furthermore, this is the only material which the silk requires, and many problems would receive a quick and easy solution could we but add from time to time just the anhydrous liquid which is taken up by the silk, leaving the water behind to receive more chloride, which again is passed to the fibre, continuing this simple process indefinitely.

* See "The Modern Asphalt Pavement" and "Origin of Asphalt" by Clifford Richardson.

† Composition and Nature of Linseed Oil. See Toch's "Chemistry and Technology of Mixed Paints," p. 80.

Now that the author has perfected processes and apparatus by means of which perfectly pure stannic chloride can readily be prepared for purposes of addition directly to the treating vat, by starting with distilled water in the vat, it at once becomes possible to subject the delicate fibres and tissues of the silk to the weighting process, under conditions of entire absence of all foreign and deleterious bodies. The tin salts and compounds received into the tissues under these conditions possess several definite features of advantage. Not only is there decidedly more lustre and uniformity imparted to the sheen, but the chemical action is uniform and regular throughout the batch. There are no adulterants which have shielded part of the fibre and caused it to take on less action or a different degree of chemicalization than at other points in the skein, nor is the true chemical reaction sought perverted in any way or complicated by the presence of substances tending to produce new and unsought compounds of a more complex nature. These complex bodies and their secondary reaction products tend definitely to destroy the strength of the silk and to render it light sensitive and slowly deteriorant.

Fig. 1 shows a diagrammatic view of the plant used for the preparation of pure stannic chloride. Pure or impure

Fig. 1.

tin-bearing material is placed in the receivers, 1; chlorine is admitted by the pipe, 2, and the product gradually accumulates in the receivers. For economical production of the material, gaseous chlorine in the form ordinarily produced, associated with more or less air and moisture, is employed, the chlorine being absorbed in the receivers. The air, which takes up some stannic chloride and also carries the sublimed hydrate due to the moisture in the gas, is received in pipe 5 and conducted to one or other of the condensers, 26, which serves the two-fold purpose of recovering nearly all the anhydrous stannic chloride contained in the vapours and air within pipe 5, and also of receiving such stannic chloride hydrate as may also be contained in these vapours. The latter is drawn off at 29, the former being received by pipe 28 at the bottom of the condenser. The pipe then proceeds to the tower, 30, where the vapours rise to the suction of fan 36, in opposition to the downwardly trickling stream of water entering at 32, a solution being readily formed and issuing from pipe 33. This solution is perfectly colourless; it has a density of about 60° B. About 4 per cent. of the total product may be represented by this solution.

One of the peculiar advantages of the product, in that it consists of anhydrous tetrachloride, is that it possesses

low specific heat and low latent heat, the vapour having a specific gravity of nearly 10, being probably the heaviest vapour known. The raw material may thus be readily treated by distillation as the second step in the process, whereby all the impurities are separated out, and left behind, only the chemically pure chloride being obtained.

One definite advance attained by the process is that this result is achieved even though extremely impure chlorine and impure tin are employed. Thus, cheap sources of both these materials are at once rendered available, which is in the greatest possible contrast to the usual methods of preparation of the solution, employing as they do only pure and highly refined tin.

The product is shipped in steel drums. This material has been found to stand for upwards of three years in an ordinary black iron container without being in the slightest degree contaminated on the one hand, and without attacking the material of the drum upon the other. Fig. 2 represents a plant of larger

Fig. 2.

capacity; the chlorine is introduced at 10, the tin bearing material being supplied from the hopper, 16, by the worm, 20. The capacity of this plant is about 500 lb. of stannic chloride hourly. Fig. 3 illustrates the chlorine drying plant. The necessity for this is brought about by the fact that by this means chlorine, which is considerably diluted with air and other gases, may be employed in the process. The chlorine together with its diluents is passed through the apparatus (Fig. 3), entering

Fig. 3.

at pipe 8, passing upwards through the refrigerator, 5, where most of the moisture is deposited, running off at pipe 80; the brine or equivalent circulation is shown by pipe 85 and receiver 72. The gas next enters the de-fogging chamber, 76, where such moisture as may be carried over mechanically is deposited and next enters the receiver, 7, being preferably heated on its way, so as to make it more absorbent. In the vessel, 7, is placed anhydrous stannic chloride, i.e., a small part of the product of the plant. As the gases pass through here, the last vestige of moisture is instantly seized upon by the chloride, the moisture being sublimed out of the chlorine; all the other gases pass next into the condenser, 9, where the gaseous chloride is trapped off and returned to the treating vessel, 7, the temperature of the jackets in condenser 9 being regulated so as to leave such gaseous

stannic chloride in the gases as has been determined by practice. The jackets, 14, covering the piping are found to be a most effectual method of preventing deposit of hydrate and thus clogging passages, which without this precaution very soon become filled with the hydrate crystals. After months of operation with this jacket it has been found that the pipes were as free from deposit as when first installed.

The readiness with which this new material lends itself to the formation or commercial production of any of the tin compounds known or required by the silk dyer is only on a par with the extreme purity of all the compounds so derived—for instance the butter of tin produced from the product is brilliantly snow-white. The solutions are also always brilliantly water-white. The stannous chloride produced by splitting off the chlorine and returning it to the process is almost a new product, the crystals being practically of ultimate purity, and the oxide thrown out of solutions made from the essence is of course perfectly pure and of extreme whiteness and brilliancy.

Scottish Section.

Meeting held at Edinburgh on February 18th, 1908.

MR. JOHN S. MACARTHUR IN THE CHAIR.

SOME NOTES ON WIJS' SOLUTION.

BY HARRY INGLE, D.S.C., PH.D.

In previous papers published in this Journal (1902, 587, and 1904, 422) I have endeavoured to elucidate the reactions taking place between unsaturated compounds and the "iodine" solutions usually employed in determining the "iodine value." It is now generally accepted that the first product of the reaction is the formation of an iodochloride and I further showed in these papers that this iodochloride is hydrolysed by the action of the water in the solution forming hydroxyl derivatives and halogen acid, and that it is reducible by the action of potassium iodide with the liberation of free iodine.

These observations led me to recommend a method of procedure in determining the "iodine value" which I fear has been misunderstood by several chemists. I stated that after doing the test in the ordinary way before adding the potassium iodide solution water should be run in so as to precipitate the chloroformic solution of the iodochlorides, thus removing them from the reducing action of the potassium iodide which should be immediately added after this separation takes place, since they are insoluble in water while potassium iodide is insoluble in chloroform. Harvey (this J., 1902, 1437) raises objections to this procedure, because he finds that when he adds water to the blank test before potassium iodide he gets a reduction in the titrable halogen. In a footnote to my second paper (*loc. cit.* 425) I briefly replied to this, but as since that was written Mr. Harvey (without having had the opportunity to peruse my reply) in the same issue, again calls this in question, I may be allowed to answer his objections at length, and at the same time clear up this point.

There is no advantage to be gained by adding water to the blank test before the potassium iodide, as there are no iodochlorides of unsaturated compounds present. Iodine chloride being soluble in both chloroform and water, is not removed from the sphere of action of either water or potassium iodide. Harvey's results with regard to the loss of titre in this case I confirmed, and stated that it was due to the decomposition of the hypiodous acid formed by the action of the water on iodine chloride. That this takes place can be shown qualitatively by mixing Wijs' solution and water in equal parts. On standing, bubbles of gas can be seen to rise from the solution, which gradually becomes redder in colour owing to the separation of free iodine. The reactions taking place may be thus represented: (1) $\text{ICl} + \text{H}_2\text{O} = \text{HOI} + \text{HCl}$. (2) $4\text{HOI} = 2\text{H}_2\text{O} + 2\text{I}_2 + \text{O}_2$. No. 1 is a reversible reaction; if we increase the amount of hydrochloric acid present in the solution, then less hypiodous acid is formed, and, consequently, there is

less tendency for No. 2 to take place. To test this point, a quantity of Wijs' solution was saturated with hydrochloric acid gas. Two lots of 15 c.c. each were measured out, and to one 100 c.c. of water was added, and the mixture allowed to stand for 5 mins., then potassium iodide was added and thiosulphate run in as usual. To the other, potassium iodide solution was added at once. No difference was observed in the two titrations, the hydrochloric acid having prevented the formation of hypiodous acid by reversing reaction No. 1. Attempts were made to collect the oxygen gas evolved by reaction No. 2, but the apparatus at my command was not sufficiently delicate to deal with the very small quantity evolved. The change of colour of the solution due to the separation of iodine and the fact that a gas is evolved seem to me to be sufficient evidence of the truth of this view. To test the matter further it was argued that, as the rate of decomposition of hypiodous acid into iodine and oxygen must depend upon the concentration, if a small quantity of water were added to Wijs' solution the loss in titrable halogen should be greater than with a larger quantity. The following experiments were made to test this:—

(1) 15 c.c. of water was added to 18 c.c. of Wijs' solution. After 45 minutes, 10 c.c. of potassium iodide solution and 100 c.c. of water were added. Thiosulphate solution required = 27.95 c.c.

(2) 18 c.c. Wijs' solution and 100 c.c. of water, stood 40 mins. followed by 10 c.c. of potassium iodide. Thiosulphate required = 28.6 c.c.

(3) 18 c.c. of Wijs' solution. Blank test 10 c.c. of potassium iodide and 100 c.c. of water. Thiosulphate required = 29.2 c.c.

Nos. 1 and 2 reddened slightly immediately the water was added, and finally turned very red; little gas was evolved in either case. These results are in exact agreement with what the theory demands.

Harvey's contention that the reduction of titre in the blank test may be due to substitution in the acetic acid by the action of the free iodine and iodic acid does not appear to me to be sound, for it is impossible for iodic acid to exist in presence of hydrochloric or hydriodic acid, since the following reactions take place:

Neither does it appear likely that any iodic acid can exist in Hübl's solution for the same reason.

The explanation of this loss of titre which I have given appears to me to meet the case.

Iodine value of turpentine.—In the *Jahrbuch der Chemie* (1904, p. 435) Dr. Lewkowitsch criticises the results. I published in my 1904 paper for the iodine value of turpentine. On page 423 I gave the iodine value of American turpentine, pinene (b.p. 156–157°) by modified Hübl as 374, the theoretical value, and by modified Waller's solution as 242. On page 425, in the same paper, I recorded an iodine value by Wijs' method (water first), of 355 while adding potassium iodide first I obtained an iodine value of 253. I wish to here explain that the turpentines examined by Hübl's and by Wijs' solutions were not the same. In the first case, a redistilled pure turpentine was used, while in the latter a turpentine boiling between 157° and 180° C. and therefore not pure pinene, was employed. Unfortunately omitted to mention this, and in the table on page 425 the iodine value of pure pinene by modified Waller's solution was inserted. I take this opportunity of correcting this, and of certifying that I have also found that pure pinene American turpentine gives the same value, namely 374, by both modified Hübl's and Wijs' method. As some discussion has taken place as to the use of the iodine value in judging the purity of turpentine, the following iodine values obtained with Wijs' solution for various turpentine substitutes may be of interest:—

Scottish shale spirit, b.p. 70°–150° C.	112
Coal tar spirit, b.p., 150°–100° C.	94
Roain spirit (crude)	263
Do. (refined)	151
Russian turpentine (crude)	234–204
Do. (refined)	292
Old sample of American turpentine	318