In order that the use of this alloy might be experimented with for this purpose, several triangles were made. This was accomplished, in each case, by twisting together the ends of three pieces of No. 13 nichrome wire, each about four inches long. The triangles made in this manner were used to support platinum crucibles, which were ignited side by side with others supported either on platinum or common pipe-stem triangles. The crucibles showed about the same loss in weight when ignited by similar means on any of the triangles mentioned. This was true whether they were ignited over a Bunsen burner, blast lamp, using city gas (containing a large amount of sulfur) or a gasoline blast lamp. The nichrome triangles, themselves, when used with city gas, either over the Bunsen or the blast, lost, at most, one milligram an hour and at times showed either a slight gain or no loss at all. When the gasoline blast was used (this gas did not contain any sulfur) the loss of either the crucibles or the triangles was not more than two- or three-tenths of a milligram an hour. One of these triangles will outlast a number of pipe-stem triangles and at the same time allow a higher temperature to be obtained in the crucibles. In fact they make a good substitute for platinum triangles and can be made for the price of a pipe-stem triangle. This article has been put on the market by H. C. Stoelting & Co., Chicago. R. C. BENNER.

UNIVERSITY OF ARIZONA,
TUCSON.

ON THE ACTION OF CHROMYL CHLORIDE ON INDIA RUBBER.

[PRELIMINARY COMMUNICATION.]

BY D. SPENCE AND J. C. GALLETLY.

Received November 23, 1910.

The singular reactivity of india rubber towards sulfur chloride is well known, for on the results of this activity depends the technical process of "cold vulcanization." As far as we know however the action of chromyl chloride on rubber has never been investigated, a fact the more surprising in view of the work of Etard,[1] of Bredt and Jagelki[2] and of Henderson[3] and his scholars on the action of chromyl chloride on the terpenes, and of the close relationship which was at one time supposed to exist between india rubber and the terpene hydrocarbons.

In these, our preliminary researches, we have endeavored to investigate the action of chromyl chloride on rubbers of different botanical origin. We have actually found that in every case this substance reacts with india rubber to form a perfectly definit compound of the formula $C_{10}H_{16}.2(CrO_2Cl_2)$ analogous to the compound formed by the action of

---

[1] *Ann. chim. phy.*, 22, 218 (1881). *Compt. rendus*, 116, 434 (1893).

[2] *Ann.*, 310, 112 (1899).

[3] Henderson, *J. Chem. Soc.*, 55, 45 (1889). Henderson, Gray, Smith, *Ibid.*, 83, 1299 (1903). Henderson, *Ibid.*, 91, 1871 (1907). Henderson and Heilborn, *Ibid.*, 93, 288 (1908).

chromyl chloride on the terpenes. This compound is insoluble in any of the usual organic solvents but dissolves readily in water, by which it is decomposed.

We have found that the behavior of chromyl chloride towards india rubber is not exactly similar to its action on the terpenes. In the first instance the addition of chromyl chloride to rubber is not accompanied by the same evolution of heat.[1] Even in a concentrated solution of india rubber in carbon disulfide only a mild evolution of heat occurs on the addition of chromyl chloride.

In the second place, the decomposition of the chromyl chloride derivative of rubber by water is not so complete as it is in the case of the analogous compounds of the terpenes. The chromyl chloride derivative of india rubber dissolves freely and completely in water giving a perfectly clear but dark green solution and from this solution only on heating a brown gummy flocculent mass separates. None of the decomposition products appear to be volatil in steam as they are in the case of the terpenes.

By decomposing the chromyl chloride derivative of india rubber by water and extracting the aqueous solution with ether, we have isolated in an impure state a substance with aldehyde reactions, giving a derivative with phenyl hydrazine. From the same aqueous solution we have separated an insoluble substance containing chromium and chlorine in apparently perfectly definit amounts. This latter substance is insoluble in all organic reagents and is still of complex colloidal character.

By dialyzing the aqueous solution of the chromyl chloride derivative of rubber into water the chromium and chlorine can be almost entirely removed. An opalescent, colloidal solution is obtained in this way, which remains unchanged even on boiling. From this solution, however, we have separated the two substances mentioned above, admixed with a very uninviting-looking mass of resin-like decomposition products.

From the still colloidal character of the decomposition products of the action of water on the chromyl chloride compound, it is evident that just as the action of chromyl chloride on rubber is not so vigorous, in the first instance, as the action of this reagent on the terpenes, so also the decomposition of the chromyl chloride compound of india rubber is not so complete as in the case of the corresponding compounds of the terpenes. On account of the interesting character of the products of this reaction, and of the mild oxidative nature of the same we are engaged in investigating still further the nature of the changes resulting from the oxidation of rubber by chromyl chloride. We believe that the Etard reaction will serve as a means of throwing further light on the constitution of the rubber hydrocarbon.

---

[1] See Henderson, *J. Chem. Soc.*, **91**, 1871 (1907).

Experimental.

Preparation of the Chromyl Compound.—The chromyl chloride used in our experiments was freed from chlorine as far as possible by repeated distillation under diminished pressure in an atmosphere of carbon dioxide. To a 2.25 per cent. solution of rubber in dry carbon disulfide, equivalent to 1 molecule of rubber, a quantity of chromyl chloride, representing slightly more than 2 mols. CrO_2Cl_2, in carbon disulfide (5 per cent. solution) was slowly added in small quantities at a time with vigorous agitation.[1]

The addition of chromyl chloride to rubber goes so smoothly in this way that it is unnecessary to cool the reacting solutions with ice as in the case of the terpenes.

The voluminous dark brown precipitate which quickly separates from the carbon disulfide is washed by decantation till free from chromyl chloride, drained as rapidly as possible at the pump and dried *in vacuo*.

0.202 g. substance; 0.0694 g. Cr_2O_3
$C_{10}H_{16}.2(CrO_2Cl_2)$ Calculated Cr = 23.31%
Found Cr = 23.51%

The chromium content of the product from the action of chromyl chloride on rubbers of various botanical origin was found to be as follows:

Name of rubber.	Weight of chromyl chloride compound. Gram.	Weight Cr_2O_3. Gram.	Cr found. $C_{10}H_{16}$. 2(Cr O_2Cl_2) = 23 31 Cr.
Extra Fine Para	0.296	0.1022	23.63
Island Medium Para	0.3798	0.131	23.61
Ficus elastica	0.3584	0.1224	23.35
Maniçoba	0.424	0.143	23.09
Landolphia owariensis	0.4154	0.1382	22.77

The product of the reaction is a dark brown powder insoluble in organic solvents, but readily soluble in water, by which it is immediately decomposed. It absorbs moisture on exposure to air, decomposing rapidly.[2]

Decomposition of the Chromyl Chloride Derivative of Rubber by Water.—Nine grams of the chromyl chloride compound of india rubber gave a clear but dark green solution when slowly added to 200 cc. water. Steam distillation of this solution failed, however, to give volatil products. From the solution on standing and more rapidly on boiling, a brown gummy mass separated and from this by extraction with ether or, better still, by chloroform, a resin-like substance was isolated.

---

[1] Experiments conducted using 4 mols CrO_2Cl_2 to 1 mol of rubber gave a compound containing only two mols of added CrO_2Cl_2. The removal of the resins and proteins from the rubber prior to treatment with CrO_2Cl_2 does not appear to be necessary.

[2] On account of the ease with which this compound decomposes in moist air our experiments to utilize the reaction between rubber and chromyl chloride as a method for the quantitative estimation of rubber were fruitless.

The resinous extract dissolved readily in alcohol but so far attempts to obtain crystallization have failed. The extract reduced Fehling solution, reacted with decolorized fuchsin solution, decolorized dilute potassium permanganate acidified with dilute sulfuric acid, dissolved readily in 1 per cent. sodium hydroxide solution giving an intense yellow coloration on heating. From this extract by treatment with phenylhydrazine, we have isolated in an impure state a small quantity of a crystallin compound, melting at 92° (unsharp).

The decomposition of the chromyl chloride compound of rubber by water would appear, therefore, to yield as one product an aldehyde. The brown amorphous substance left after extracting the gummy precipitate formed on boiling the aqueous solution of the chromyl compound was apparently of complex colloidal character. When boiled with alcohol till free from the last traces of the resinous by-product it is a brown powder, insoluble in all organic solvents and in dilute acid. It dissolves slowly in dilute alkali and contains chromium and chlorine in apparently definit amounts.

Decomposition by Dialysis.—Ten grams of the chromyl compound were dissolved in 200 cc. of water and the solution thus obtained was dialyzed for 48 hours in a gentle stream of water and for a further 24 hours in a stream of distilled water. A small quantity of hydrated oxide separated inside the dialysis tube but this was readily removed by filtration. The pale yellow, but somewhat opalescent, colloidal solution left after dialysis is perfectly stable even above the ordinary temperature. It was readily decomposed, however, by warming with a trace of acid. Even by passing a slow current of carbon dioxide through the solution warmed on the water-bath decomposition takes place and a light brown, gummy mass separates which consists of a mixture of the alcohol-soluble resinous products extracted by chloroform with the insoluble substance isolated directly from the aqueous solution of the chromyl compound. Some analyses for Cr and Cl of the insoluble product isolated by different means and purified as far as possible are here recorded:

	Cr Per cent.	Cl Per cent.
(*a*) Separated from aqueous solution after extracting with chloroform	4.64	....
(*b*) Aqueous solution decomposed by boiling, insoluble product separated and extracted by alcohol	4.62	4.48
(*c*) By dialysis and alcohol extraction	4.81	....
	4.44	....
(*d*) Ditto	4.40	4.22

It is useless at the present stage of our investigation to offer any explanation for the singular nature of the changes resulting from the decomposition of the chromyl chloride compound of india rubber by water.

We are now engaged in isolating the aldehyde and the insoluble chromium compound in quantities sufficient to enable us to investigate them still further.

RESEARCH LABORATORIES,
THE DIAMOND RUBBER CO.,
AKRON, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE RED AND WHITE SILVER SALTS OF 2,4,6-TRIBROMOPHENOL.[1]

BY HENRY A. TORREY AND W. H. HUNTER.

Received December 16, 1910.

Only one silver salt of 2,4,6-tribromophenol was mentioned in the chemical literature at the time we took up this research. This was prepared by Purgotti[2] from the calcium salt, and described as an orange-red precipitate. In preparing this salt by precipitation of a solution of the sodium salt with silver nitrate in excess, we happened to leave a partly washed red precipitate standing on the filter for some hours; when we came to finish the washing, we found it had become completely decolorized, with the exception of some particles which had dried on the edge of the filter. A determination of silver in the air-dried white salt indicated that it was isomeric with the red salt, which was amply confirmed by later analyses of pure specimens.

A study of the conditions under which the white isomer was formed showed that it could be obtained from the red compound by carrying on the precipitation from very dilute solutions, or from a boiling solution, or by solution of the red salt in a little ammonia, and precipitating the white salt from this solution by the addition of more silver nitrate solution. Of these methods, the last is the only one which gives us a pure white salt, and can be used to advantage as a method of preparation. It also furnishes us with a probable explanation of the formation of the white salt from the red when exposed to the air of the laboratory, which may well have contained ammonia.

At this point of our work, a preliminary paper was published,[3] and this called forth immediately a paper[4] from Hantzsch's laboratory, in

---

[1] This research was suggested by the late Professor Henry A. Torrey and the experimental work was done under his direction but the explanation of the observations and the writing of the paper were deprived of the benefit of his supervision by his too early death. C. L. JACKSON.

The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by William Hammett Hunter.

[2] *Gazz. chim. ital.*, 16, 527 (1886).

[3] *Ber.*, 40, 4332 (1907).

[4] *Ibid.*, 40, 4875 (1907).