

An  
Investigation  
of the  
Action of  
Chloride of Sulphur  
upon  
Spirits of Turpentine,  
by  
Charles N. Waite  
and  
Albert H. Low.

Mass. Inst. Tech.  
1876.

The following research was begun by Messrs Waite and Low and carried on by them conjointly until various comparatively pure products had been obtained, consisting mainly of sulpho compounds, chlorine compounds and terpenes: Mr. Waite then directed his attention to the sulpho compounds, while the terpenes and bodies containing chlorine were studied by Mr. Low.

Part First

by

Albert H. Low.

Chapter First.

Description of the joint work of  
Messrs Waite and Low.



1

The Action of  
Chloride of Sulphur on Spirite of Turpentine.

It is a well known fact that by means of the dichloride of sulphur many oils and similar substances may be "vulcanized" or converted into products more or less resembling vulcanized caoutchouc.

"If to a vegetable oil there is added one thirtieth of its volume of chloride of sulphur, the latter dissolves in the oil, the mixture becoming heated and quite viscous. If one tenth its volume be added to the oil, the temperature rises from  $50^{\circ}$  to  $60^{\circ}$  C and the mass suddenly becomes stiff without losing its transparency. This product has little elasticity and contracts somewhat after stiffening. If it is allowed to soften in distilled water it becomes opaque white. After a few days it is changed into a white, friable, elastic mass."<sup>(1)</sup>

1. Dingler. Pol. J. CLI. p. 136.

"Rocheleder has investigated the action of chloride of sulphur on the fat oils. If chloride of sulphur be added drop by drop to provence oil, this, by further treatment, hardens to a yellow, translucent jelly, not acted upon by ether, alcohol or water.

It is as elastic, and more transparent than caoutchouc at the ordinary temperature."<sup>(1)</sup>

Ms. Perra<sup>(2)</sup> has noted the effect of chloride of sulphur on linseed oil and gives the following as the results of his investigation:

"One hundred parts of linseed oil, treated with twenty five parts of Chloride of sulphur, give a hard product. If only fifteen or twenty parts of chloride of sulphur are taken, a soft product results. Five parts of chloride of sulphur merely thicken the oil without rendering it stiff."

+++++ "All the products that can be obtained by the mixture of chloride of sulphur and linseed oil are perfectly transparent, if care is taken to put the manufactured articles in a dry case or warm

1. Dingler, Pol. J. vol. CXI, p. 159.

2. Comptes Rendus. Nov. 1858, No. 22.



3  
place, by which treatment the excess of chloride of sulphur is driven off and moisture is prevented from injuring the transparency by decomposing the chloride of sulphur and precipitating sulphur."

"The hard compound of linseed oil and chloride of sulphur is not attacked at all by atmospheric agencies; I have exposed it for several years to the action of the weather."

"It is well known that vulcanized, i. e. sulphurized rubber is soft in the cold. The above compounds, which have been considered as oil, vulcanized by chloride of sulphur, are stiff and brittle and retain for some time a very marked odor"

In the so-called "Parkes Process" of vulcanizing caoutchouc, the Inventor employs the following method:<sup>(1)</sup>

"In carrying out my improvements I employ

---

1. No. 11,147 Eng. Patents 1846.

4  
bisulphuret of carbon or sulphuret of carbon, or I employ coal naphtha or turpentine or any other suitable solvent of caoutchouc, and I dissolve in either of them (preferring bisulphuret of carbon) the other matters hereafter described, and produce thereby, in a greater or less degree, the improvements I contemplate in this portion of my invention, and which improvements, for the sake of brevity, I will hereafter call "the change".

"I take forty parts of bisulphuret of carbon and add to it one part of chloride of sulphur or hypochloride of sulphur, prepared as neutrally as possible, and well mix them in an earthen or other suitable vessel and I immerse caoutchouc in sheets or other forms in this mixture, allowing them to remain therein a longer or shorter time according to the thickness or substance of the article, but I find that for general purposes a sheet of one sixteenth of an inch in thickness is sufficiently changed in from one to two minutes; but in case the caoutchouc is of considerable thickness, I use a smaller proportion of chloride of sulphur, that it may



act more slowly upon the mass, as I have found that a strong solution, when in contact for a long period, acts prejudicially on the surface."

It will be noticed that the inventor claims to be able to employ a mixture of turpentine and chloride of sulphur as a vulcanizing liquid.

He implies that the naphtha, turpentine or bisulphide of carbon, as the case may be, acts simply as a solvent towards the chloride of sulphur besides being a solvent of caoutchouc:—that no decomposition results from the mixture. This is true as regards bisulphide of carbon, but it would seem that as chloride of sulphur produces such a marked effect on linseed and other oils, entirely changing their nature, there would be some such action in the case of spirits of turpentine.

It was with a view of settling this point and determining, as fully as possible, the nature of such action, if any, that the present research was undertaken.



The spirits of turpentine employed was the American turpentine, and was boiled previous to use, to remove water and hydrates. The boiling point of the turpentine thus purified was  $160^{\circ}\text{C}$  at the ordinary pressure. Its Sp. gr. was .867.

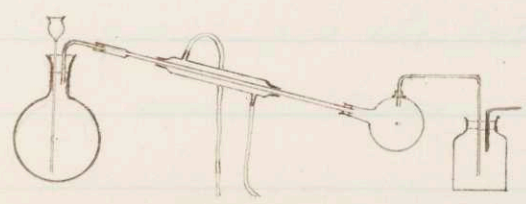
It had a strong right-handed rotary power.

The chloride of sulphur used was the ordinary dichloride and was not purified, hence it may have contained an excess of sulphur.

It was a clear, brownish yellow liquid.

About fifty c.c. of the spirits of turpentine were placed in a flask of about 300 c.c. capacity.

The flask was arranged with a thistle tube and connected with a Liebig condenser. The condenser connected with a small tubulated receiver which in turn communicated with a small Wolf's bottle containing caustic soda solution.



About five c.c. of chloride of sulphur were now poured very gradually through the thistle tube into the flask. This immediately produced a violent boiling, white, acid vapors being evolved from the open end of the apparatus.

Heat was applied to the flask as soon as the first commotion had subsided, by means of a water bath, in which was immersed a thermometer.

The temperature was raised very gradually. At  $100^{\circ}\text{C}$  the mixture did not boil, but simply darkened in color. The water bath was then removed and a sand bath substituted. The heat was now increased until the mixture boiled. The vapors thus produced would not rise out of the flask, but continually condensed and fell back. Of course nothing collected in the receiver.

The thistle tube was then replaced by a common tube, reaching nearly to the bottom of the flask and by means of which steam was passed through the heated mixture.

This at first caused vapors to come over which



8  
condensed and collected in the receiver in the shape of two colorless liquids of different densities. The heavier appeared to be water and the lighter resembled the original spirits of turpentine although the odor was somewhat different.

As the heat increased, a yellowish, gelatinous substance began to collect in the condenser.

It accumulated in the lower end of the condenser in such an amount as to finally choke up the passage. It thus became necessary to use some other form of condenser: accordingly the Liebig apparatus was removed and a tube of large diameter, not cooled, substituted for it.

The current of steam was now discontinued and the heat increased. The mixture in the flask which had now become very dark and viscous, bumped violently at intervals. Hoping to stop this action and cause the liquid to boil quietly, the heat was still further increased. Just as the desired point appeared to have been reached, the flask burst. The mixture took fire, and the smell was similar to that of burning rubber.

The liquid which had collected in the receiver

was of a yellowish color and possessed a very penetrating and disagreeable odor.

The substance which had clogged the Liebig apparatus was soft like butter and had a peculiar aromatic odor. When pressed between blotting paper there remained a white, crystalline solid somewhat resembling common camphor. It was soluble in alcohol and could be easily sublimed.

The results of the above operation seemed to show that there was an excess of turpentine in the mixture and it was therefore deemed advisable to repeat the distillation, using a larger proportion of chloride of sulphur and at the same time employing a lower temperature: the vapors were, as before, to be driven over by means of a current of steam.

Accordingly about 12 c.c. of chloride of sulphur were added gradually to about 50 c.c. of the turpentine, the flask being placed in a vessel of water during the mixing to keep it cool.

The flask was then connected with the rest of the apparatus, the Liebig condenser being used



in the first part of the operation to condense the more volatile products. The flask was heated by means of a salt bath and the temperature raised gradually, to about  $102^{\circ}\text{C}$  at which point it was kept throughout the remainder of the distillation. But little of the turpentine-like liquid came over which seemed to indicate that about the right amount of chloride of sulphur had been taken. Soon the gelatinous substance began to collect in the condenser and it was therefore necessary to replace it by a tube of large diameter as before. A considerable amount of the gelatinous body was thus obtained and a thick, brownish liquid was left in the flask.

An objectionable feature of the above process was that the products of distillation were mixed with more or less water, and therefore another method was adopted which dispensed with the current of steam. The apparatus was simply a small tubulated glass retort, which connected directly with a receiver and was heated with the naked flame of a Bunsen burner. The proportions of spirits of turpen-



71  
tine and chloride of sulphur used were the same as in the last operation.

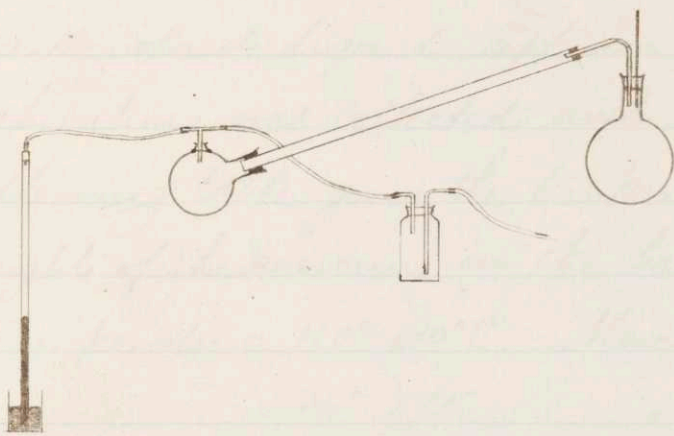
About the first thing to come over was the camphor-like substance; then a colorless or slightly yellow liquid distilled, which was followed, on increasing the heat by a dense reddish liquid which gave color to the whole contents of the receiver. After thus distilling until the residue in the retort was very dark and dense the operation was stopped. The blackish mass in the retort was somewhat soft and gummy even when cold and resembled wood tar. It had a strong odor.

The above process was repeated several times until a litre or more of the red distillate had been collected. This was then bottled, and labelled "A".

It possessed a strong rubber-like odor at first but after standing a few days, decomposition set in and a quantity of sulphuretted hydrogen was developed which was recognized by its odor and by its action on lead paper.

106

The next step was to subject A to distillation, and for this purpose an apparatus was devised when by a partial vacuum could be secured and thus allow the work to be carried on at a lower temperature. A flask was used which connected with a small tubulated receiver by means of a condensing tube of large diameter. In the tubulure of the receiver was fitted a T piece, one arm of which connected with a Richards' aspirator, and the other was attached to an ordinary barometer tube dipping into mercury in order that the degree of rarification might be observed.



In the neck of the flask was placed a thermometer, in order that the temperature at which the



vapors came over might also be known.

In fitting up the apparatus, common corks were used in preference to those made of rubber as chloride of sulphur attacks the latter.

The flask was heated with the naked flame of a Bunsen burner.

Only small quantities of A were operated on at a time and it therefore required five distillations to use it all. The distillate was of a yellowish color and would probably have been colorless had not slight portions of the liquid in the flask spattered over. This distillate was called "B".

The dark colored liquid left in the flask after all these operations was collected and labelled "C".

The following table gives the temperatures and also the heights of the mercury in the barometer tube.

1st time,	Temperature	110°-130°C.	Mercury,	26.5 inches
2nd time,	"	141°-170°	"	24.5 "
3rd time,	"	137°	"	27.3 "
4th time,	"	162°-158°-165°	"	19.5-23.5-24 "
5th time,	"	117°-135°	"	27 "

The distillate B was now subjected to distillation in a partial vacuum as before. The product was a yellowish liquid and was marked "D".

Most of D came over between 140° & 150°C, the mercury in the barometer tube standing at 23 inches.

The boiling point of D at the ordinary pressure was about 205°C.

Before going any further in this direction, it was thought advisable to distil some of the original mixture of chloride of sulphur and spirits of turpentine in a partial vacuum, and thus, by not being obliged to employ so high a temperature perhaps avoid one or two distillations and arrive quicker at the liquid D.

A mixture of about 100 c.c. of spirits of turpentine and 30 c.c. of chloride of sulphur was operated upon. The distillation was repeated four times. The following table indicates the temperature and pressure in each case:

1st time,	Temperature,	121°-170° C.	Mercury,	27.5 inches.
2nd time,	"	150°-170°	"	21.5 "
3rd time,	"	100°-170°	"	25.7 "
4th time,	"	100°-140°	"	24.5 "



In each case it was noticeable that the larger part of the vapors came over at about 140°C.

At 170°C the liquid in the retort would thicken and froth up considerably and therefore, in the last distillation the temperature was not increased above 140°C.

The distillate was of a reddish color and was marked "E". The dark, tarry residue in the flask was saved and marked "F."

Some of E was now redistilled and it was found that with the mercury in the gauge standing at 28 <sup>3</sup>/<sub>4</sub> inches, it boiled at 90°C but when the mercury fell to 21.5 inches, E would not boil below a temperature of 145°C.

The distillate was a yellowish liquid with acid fumes and was labelled "G."

Its boiling point, at the ordinary pressure was found to be the same as that of D; 205°C.

This was what was expected.

As a quantity of B still remained on hand this was now distilled to obtain more of D or G.



As B bumped considerably when a vacuum was employed, none was used this time and the boiling proceeded more regularly.

A considerable quantity of D and G had now been accumulated. This was redistilled from a common retort, the neck of which was inclined upwards, and a colorless product, H, obtained.

The dark tarry residue C, which was left behind when A was distilled, was now distilled <sup>partial</sup> in vacuo and the heavy vapors were driven over by means of a current of air which was allowed to bubble through the liquid in the flask.

With the mercury in the gauge standing at 28.5 inches the vapors were thus driven over at a temperature of 110°-140°C.

The product was a yellowish liquid containing a large quantity of the gelatinous, camphor-like substance diffused through it. It much resembled D and G and was marked "G'."

A reddish liquid remained in the flask.

It was darker and somewhat more tarry than the original C.

This residue was now mixed with E' and redistilled in a partial vacuum with the aid of a current of air. With the mercury in the gauge standing at 26 inches, the product came over at  $165^{\circ}$ - $198^{\circ}$  C.

A red liquid, resembling B, was thus obtained, and was marked "B'". The tarry residue left in the flask was thrown away.

H was now purified by two distillations and a colorless liquid "I" obtained. The residues in each case were reddish liquids and were mixed with B' and redistilled in a partial vacuum with a current of air. The distillate was a red liquid and was marked "J".

Heavy liquids were so easily distilled in a partial vacuum by means of a current of air, that it was deemed possible to obtain all the volatile products from the original mixture of spirits of turpentine and chloride of sulphur in one operation.

This method was accordingly tried and found to succeed very well. The temperature was finally raised as high as  $230^{\circ}$  C and the distillation was



continued until nothing but a coke-like substance remained in the flask. The distillate was a red liquid containing some of the camphor-like substance previously mentioned.

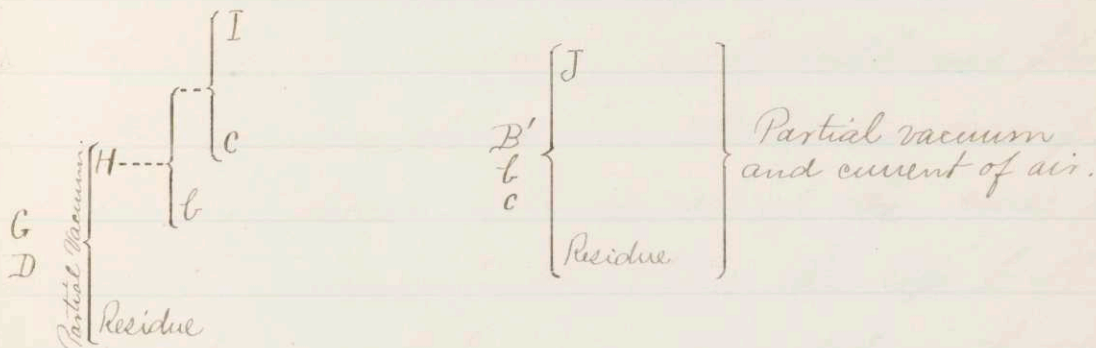
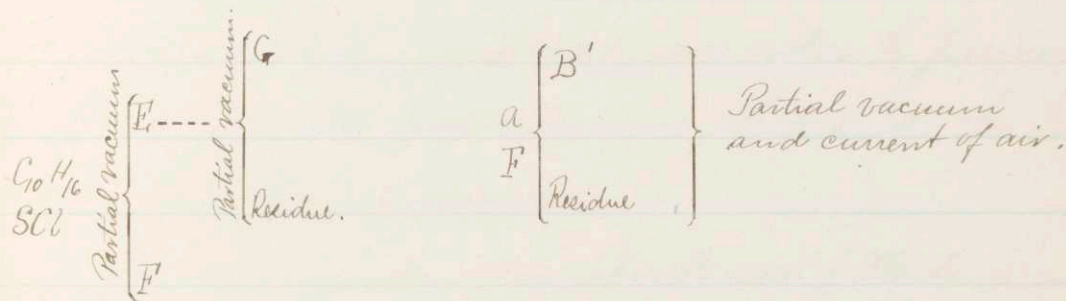
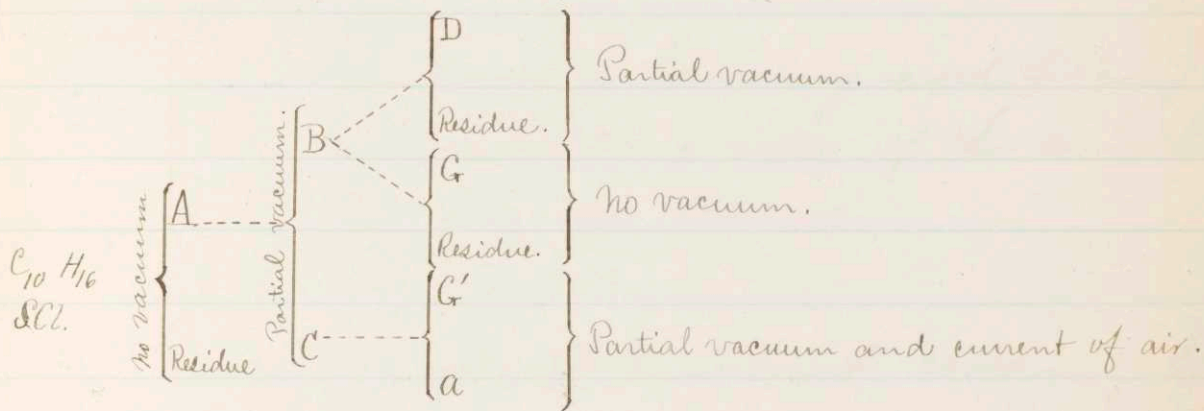
It will be remembered that in previously distilling the original mixture in a partial vacuum without a current of air, it was found to be impossible to drive the the operation to the end, on account of the frothing up of the liquid.

The red distillate obtained as above, was now mixed with the other reddish colored liquids J, G' and E, and redistilled to get a purer product which was called "K." K contained much of the camphor substance as did also the red, liquid residue "I," which was left in the flask.

By subjecting K and I, to a considerable degree of cold, the camphor-like body crystallized out and was then separated from the liquids by filtration. A large quantity of the impure product was thus obtained, which was reserved for subsequent analysis &c.

The work done thus far may be tabu-

lated as follows. In each case the lower product on the right of a bracket is a residue.



$C_{10}H_{16}$ SO <sub>2</sub>	Red liquid	Partial vacuum and current of air.
	Coke	

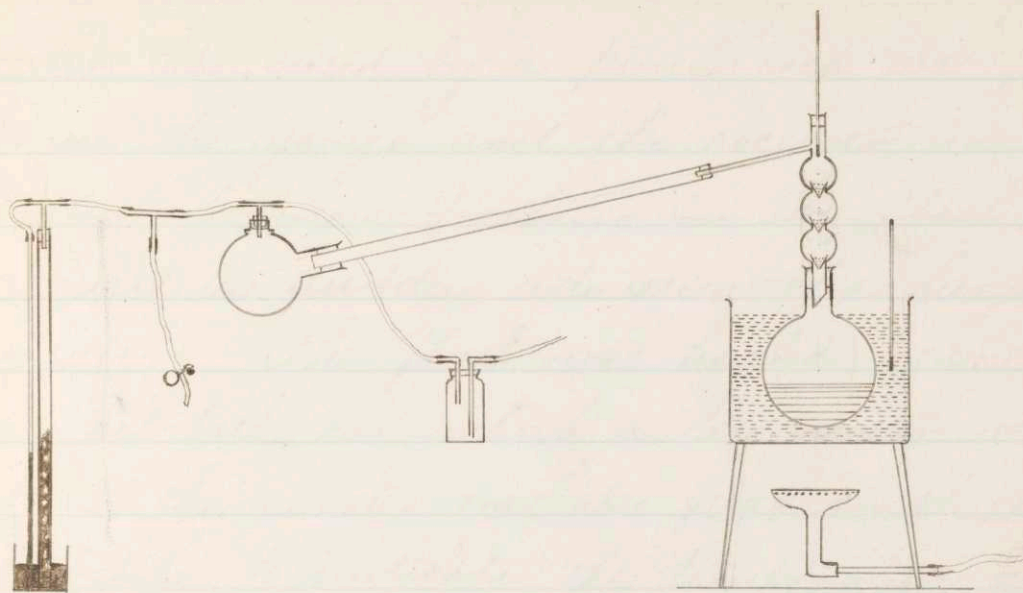
Red liquid G' E J	K	From K and I, by cooling and filtering, a considerable quantity of the camphor- like body was obtained.
	I	

It was now desirable to submit certain of the above liquids to fractional distillation. A partial vacuum was to be employed, in order to prevent "cracking" as far as possible. To this end the following apparatus was arranged.

In the neck of a flask was fitted a straight piece of glass tube in which three bulbs were blown.

In the lower neck of each bulb was placed a diaphragm consisting of a platinum cone pierced with fine holes. The apices of the cones pointed downwards. Immediately above the top bulb a small delivery tube communicated with the condenser. A small tubulated receiver was used, in the tubulure of which was fitted a T piece





which communicated with a mercury gauge and with a Richard's aspirator.

In the previous distillations in vacuo some trouble had been experienced in keeping the degree of rarification constant and therefore the following method was this time adopted: Near the bottom of the gauge tube was filed a horizontal aperture through which air would enter when the level of the mercury in the cup became sufficiently lowered, i.e. when a certain degree of rarification had been attained in the tube above and which was measured by means of a smaller gauge tube

placed beside the first. This arrangement succeeded very well. By means of a T piece a rubber tube closed by a pinch-cock was placed between the gauge and the receiver in case a violent boiling or frothing in the flask should require the sudden admission of a large amount of air. The flask was heated by means of an oil-bath in which a thermometer was placed.

A thermometer was also fitted in the top of the bulb-tube, to indicate the temperature of the vapor coming over. The condenser was simply a long glass tube of large diameter, not cooled.

The above arrangement, properly managed gives excellent results and very complete separations may be made by means of it.

For the sake of brevity, the fractional distillations which were now made are tabulated as follows:

I K	}	M	Oil bath 171° - 200° C.
			Vapor thermometer 108° - 160° C.
			Mercury gauge 426 mm.
		N. Residue.	

M { O Came over at 138°-145° C.  
 P " " " 145°-155°  
 Q " " " 155-160°  
 R Residue. Gauge, 426 m.m.

N { S Came over at 110°-125° C.  
 L { T " " " 125°-145°  
 R { U " " " 145°-175°  
 V " " " 175°-185°  
 W Residue. Gauge, 660 m.m.

U was redistilled and everything that came over below 150° was mixed with T. The remainder of the liquid was then mixed with V.

V { Product, Came over at 150°-160° C.  
 Product, " " " 160°-170°  
 Residue. Gauge, 660. m.m.

The above products were all liquid at the ordinary temperature and varied in tint all the way from colorless to yellow and even red.



Up to this point Messrs Waitt and Low had worked in common, but it was now desirable to study certain of the products more closely and with reference to their composition: accordingly the liquids of higher boiling point containing sulphur were investigated by Mr. Waitt and the lighter liquids and chlorine compounds by Mr. Low.

Chapter                  Second.

Examination of the  
Chlorine Compounds and Terpenes.

From many of the products and residues of both the fractional and other distillations, considerable quantities of the camphor-like substance before mentioned had been separated by cooling and filtering, and it was therefore now proposed to purify it and determine its composition and physical properties.

By crystallizing from hot alcohol several times and subsequently fusing it, the camphor was obtained in what was supposed to be a pure condition.

It was now tested for and found to contain chlorine, but no sulphur.

The melting point, somewhat roughly determined, was found to be  $115^{\circ} \text{C}$ .

It was now analyzed quantitatively for carbon and hydrogen by burning in oxygen, the tube being packed in the following manner:



- a.a.a., asbestos plugs.
- b., boat containing the camphor.
- c., oxide of copper.
- d., silver foil for the detention of chlorine.



Six analyses were made with the following results.

C.	66.36%	66.20	64.25	—	68.65	68.43
H.	9.73%	9.51	9.64	9.16	9.79	9.69

It was now examined quantitatively for chlorine by heating in a tube with quicklime and finally weighing the chlorine as AgCl.

Two analyses were made, as follows:

Cl.	21.20%	21.14%
-----	--------	--------

The above analyses were all more or less unsatisfactory, partly from supposed loss in working with so volatile a solid and partly from the now presumed presence of impurities.

The substance was therefore further purified by sublimation and again analyzed with greater care. The results seemed to point to the formula  $C_{10}H_{16}.HCl$ .

	Theoretical.	Found.	Found.
C.	69.57%	69.12%	68.65%
H.	9.85	10.47	10.19
Cl.	20.58	20.55	20.42

It was now necessary to determine the vapor-density of the substance in order to calculate the molecular weight.

	Theoretical	Found.
Mol. wt.	172.5	171.8

Its formula was therefore now considered sufficiently established as  $C_{10}H_{16}.HCl$ .

It was found by experiment to possess a slight right-handed rotary power.

It sublimed, when heated, in colorless acicular crystals which could not be rubbed to powder but were of a pitchy nature. The odor of the substance was somewhat like that of common camphor.

Bodies of the composition  $C_{10}H_{16}.HCl$  have heretofore been prepared by operating upon oil of turpentine with chlorhydric acid gas &c., but none of them appears to have exactly the same physical properties as the present substance.

"By slowly passing chlorhydric acid gas over terebene, cooled by water, the terebene is changed into a crystalline mass of terebene chlorhydrate  $C_{10}H_{16}.HCl$ . + + + In order to obtain the pure tere-



lene chlorhydrate it is best to bring the impure product into a spacious balloon, displace the air by dry chlorhydric acid gas, and then melt the substance by placing the whole apparatus in a sand bath which is in turn heated by means of a water bath.

The terebene chlorhydrate sublimed in the manner forms a crystalline crust or feathery crystals which can be rubbed to powder. It possesses a camphor-like odor, melts at  $125^{\circ}$  and is optically inactive. By cold water it is decomposed into HCl and crystalline camphene  $C_{10}H_{16}$ . By boiling with water only liquid products are obtained.

From the warm solution in absolute alcohol terebene chlorhydrate separates out on cooling in white leaves, if the solution has not been heated above  $55^{\circ}$  or  $60^{\circ}$ . Even in this case a slight decomposition takes place. By boiling the terebene chlorhydrate with alcohol it becomes quickly decomposed and a liquid product results which does not give a crystalline chlor-



hydrate with HCl."<sup>(1)</sup>

This "terebene chlorhydrate" differs from the present substance in its melting point, in being optically inactive, in being decomposed by cold water and in admitting of being rubbed to powder.

Concerning the action of chlorhydric acid upon spirits of turpentine Berthelot<sup>(2)</sup> says:

"Chlorhydric acid unites directly with spirits of turpentine and forms several compounds according to the conditions of the reaction, as follows:

- A crystalline monochlorhydrate,  $C_{10}H_{16}.HCl.$
- A liquid monochlorhydrate,  $C_{10}H_{16}.HCl.$
- A crystalline dichlorhydrate,  $C_{10}H_{16}.2HCl.$

Besides these there are the two compounds which result from the union of the last with each of the first:



Let us show how the different compounds can be prepared.

Monochlorhydrates. The two monochlorhydrates are ob-

---

1. Jahresbericht. 1873., p. 372.  
 2. Traité Élémentaire de Chimie Organique. 1872, p. 135.

27  
tained in a state of mixture when a current of chlor-  
hydric acid gas is passed through spirits of turpentine.

After several hours, the liquid thickens into a  
crystalline mass impregnated with liquid. The  
solid and liquid have the same composition and  
possess the same rotary power.

The solid monochlorhydrate may be isolated by  
pressing out the liquid, and purified by crystal-  
lization from alcohol.

It is white, crystalline and possessed of an odor  
and physical properties analogous to those of cam-  
phor, whence the inexact name of "artificial cam-  
phor" which has heretofore been applied to it.

It melts at  $115^{\circ}$  and boils at about  $208^{\circ}$ . It  
sublimes easily and at the ordinary temper-  
ature. Its rotary power is  $-31^{\circ}$ . It is quite stable.

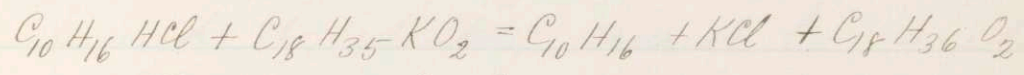
However, under the influence of alkalis or alka-  
line salts, acting at about  $200^{\circ}$  -  $250^{\circ}$ , the solid mono-  
chlorhydrate can be separated into HCl and a  
hydrocarbon. This hydrocarbon possesses different  
properties according to the conditions under which



it has been reproduced.

If the decomposition of the chlorhydrate is effected very carefully by heating it with stearate of potassium or with dry soap, to 200°-220° for twenty hours in a flask with a long neck, a crystalline hydrocarbon is obtained, which is optically active.

It is terècamphène:



++++ Treated with chlorhydric acid gas, terècamphène is entirely changed into a crystalline monochlorhydrate, isomeric, but not identical with the chlorhydrate obtained from turpentine; in fact it possesses a contrary rotary power, equal to +32°."

The first of Berthelot's solid monochlorhydrates resembles very closely the substance in question, but it has a left-handed rotary power. However as he worked with the French spirits of turpentine obtained from the pinus maritima, which possesses a left-handed rotary power, and as in this investigation the American, right-handed, spirits, obtained from the pinus australis has been used, this difference in rotary power is probably the only one which exists between the two hydrochlorides.



The second of Berthelot's solid monochlorhydrates, prepared from *léicamphène*, possesses a right-handed rotary power and may be identical with the hydrochloride obtained in this research, but as he does not give the other physical properties of his compound the identity cannot be considered as established.

Work on the camphor-like substance was carried no further and the attention was turned to the liquid O, obtained as the first product in the fractional distillation of M. (see page 23).

O was a colorless, mobile liquid boiling at about 162°C at the ordinary pressure.

Its index of refraction was 1.474.

In a Soleil saccharimeter it showed a right-handed rotary power of 39.5°.

It was now redistilled in a partial vacuum until about one half had come over. The distillate was a colorless, mobile liquid, possessed of an aromatic odor. It was marked "X".

In the saccharimeter, X gave a right-hand-

ed rotation of  $43.5^\circ$ ;

The residue in the flask was a yellowish liquid possessing a right-handed rotary power of  $40^\circ$ .

It was labelled "Y".

Y was redistilled in a partial vacuum and a colorless product "Z" obtained. The residue in the retort appeared to be crystals of  $C_{10}H_{16} \cdot HCl$  saturated with a reddish liquid.

Z had a rotary power of  $34^\circ$ .

For want of a suitable apparatus for determining the specific rotary power of the various products it was necessary to use a saccharimeter, and thus only comparative results were obtained.

The following is a list of the substances examined in this way; they were all right-handed.

Spirits of turpentine	$141.1^\circ$
O	$39.5^\circ$
X	$43.5^\circ$
Y	$40.0^\circ$
Z	$34.0^\circ$
P	$34.0^\circ$
Q	$37.0^\circ$

$\alpha_D^{20}$  35.6°

T 59.5°

$C_{10}H_{16} \cdot HCl$  was dissolved in alcohol at the ordinary temperature and the saturated solution possessed a rotary power of 5°.

X was analyzed with the following result:

C. 87.92%

H.  $\frac{12.08}{100.00}$

This indicated that the liquid was probably an impure terpene -  $C_{10}H_{16}$  - the theoretical composition of the pure product being,

C. 88.25%

H.  $\frac{11.75}{100.00}$

Z, which had a higher boiling point, was found to contain chlorine, but this might have been due to the presence of  $C_{10}H_{16} \cdot HCl$ , a quantity of which remained in the flask after distilling off Z.



Beyond this point nothing further was accomplished, but the work was brought to a close on account of lack of time to continue it.

In addition to the products described, certain sulpho-compounds were obtained from the original mixture of Chloride of sulphur and spirits of turpentine. These compounds were made the subject of a separate research<sup>(1)</sup> and are therefore not considered in this paper.

The results of the investigation herein described show conclusively that chloride of sulphur and spirits of turpentine can not be mixed without producing mutual decomposition, - even though the mixture be made at a low temperature and very gradually, by dropping the chloride of sulphur into the spirits of turpentine, - and that sulpho- and chlorine compounds are formed together with isomers of spirits of turpentine. Therefore the fact of Parkes having used spirits of turpentine as claimed, in his process for vulcanizing caout-

1. Thesis of Mr. C. N. Waite, M. I. T., 1876.

chance seems highly improbable.

It may here be stated that the progress of the research was somewhat hampered by the lack of suitable arrangements for carrying on the work, necessitated by the inadequately small amount of floor room allotted to the department.

In conclusion, I desire to tender my earnest thanks to Prof. C. H. Wing for the valuable suggestions and generous assistance accorded during the course of the investigation, and to express my hearty appreciation of the same.

Respectfully submitted,  
Albert Howard Low.

Part Second,

By C. N. Wait,

Chapter I. Remarks on the joint  
works of Messrs. Wait and Lovv.

Chapter II. Consideration of Sulpho  
Compounds, by C. N. Wait.



This research was undertaken, in the hopes of throwing some light, on the action which takes place in the so-called "vulcanization".

It has been known for many years, that, if chloride of sulphur be allowed to act on many animal<sup>(1)</sup> or vegetable oils<sup>(2)</sup>, and on caoutchouc, it produces a change in them, called vulcanization, whereby the substance becomes hard and brittle, or soft and elastic, according to the proportion of the reagents used.

---

(1) Rochleder, Dingl. pol. j. CXI 159.

(2) Roussin " " " CLI 136

Kera<sup>(1)</sup> found that if one part of chloride of sulphur be added to twenty parts of linseed oil, the mass heats up and becomes viscous. If one part in five or six, the mass becomes gelatinous, and if one part in four the product is hard.

The first product is soluble in all the solvents of linseed oil; the others only swell and lose a certain amount of sulphur.

These bodies seemed to have all the properties of ordinary caoutchouc.

Chloride of sulphur was used by Parkes<sup>(2)</sup> in a patent taken out

---

111 Dingl. pol. j. C L I 138.

121 \* 11,147 Eng. Patents. 1846.

Reperit. of pat. Inv. 1847.

Rapport de l'Exposition de 1851, Balard.



by him in 1846. for the vulcanization of caoutchouc.

The process may be briefly stated as follows. One part of chloride of sulphur was dissolved in forty parts of bisulphide of carbon, and the article to be vulcanized was plunged into this bath, for from four to eight minutes, according to thickness, and then hung in a warm dry place to expel the excess of chloride of sulphur.

The bisulphide of carbon was used merely as a vehicle for the chloride of sulphur, also to soften the surfaces of the article, and allow it to be acted on more readily, and as a diluent of the chloride of sulphur, thus rendering the action more regular and gentle.



He claims that the change may be effected by means of the chlorides, sulphates, sulphides, nitrates, and phosphates of the metals and earths, but preferably of sulphur, carbon, arsenic and antimony, but it is not known that it can be effected by anything except sulphur and allied element, as selenium etc.

Exactly what the change is which takes place, in all these cases is not known, since in the case of the linseed oil investigation, the investigator did not try to determine the composition of his product, and in the case of caoutchouc, the materials acted on are always impure, and hence the product obtained has no constant composition.

If some pure caoutchouc, as prepared by Faraday,<sup>11</sup> were acted on by chloride of sulphur, it is possible that a product might be obtained of sufficient purity for analysis.

However, this fact is known, that in all these cases, chlorhydric acid is liberated, and it may be surmised, that the sulphur takes the place of the hydrogen, which goes off in the chlorhydric acid.

When chloride of sulphur is mixed with oil of turpentine a very violent action takes place, and fumes of chlorhydric acid are given off. In one instance when five or six cubic centimetres of chloride of sulphur were

---

See Faraday's *Res. Researches in Chem. & Phys.*



added to fifty cubic centimeters of oil, at once, the reaction had almost the violence of an explosion, blowing nearly the entire contents out of the flask. The mass thickens and turns a dark red color. Even when thirty parts of chloride of sulphur are added to one hundred parts of oil, the mass does not become thicker than cold molasses, and hence may be purified by fractional distillation, and rendered fit for analysis.

From the study of this reaction it is hoped that some clue may be found to vulcanization.

The turpentine used for this research was the American turpentine (from *Pinus australis*.) having sp. gr. of .867, and boiling at  $160^{\circ}$ .



It has a strong righthanded rotation. It was first boiled in order to free it from water and hydrates.

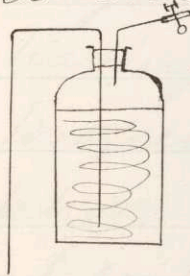
The chloride of sulphur was the ordinary commercial article, of a reddish yellow color, and probably containing sulphur in excess.

The experiment was first tried, of adding ten parts of chloride of sulphur to one hundred of the hydrocarbon, but on distilling, a large amount of unchanged hydrocarbon came off.

On increasing the proportion of chloride of sulphur, this excess of hydrocarbon was diminished, until with the proportions thirty to one hundred, the excess was very small indeed. As it was advisable,

always, to have an excess of the hydrocarbon present, these proportions were not exceeded.

The chloride of sulphur must be added very cautiously, and the vessel containing the hydrocarbon must be placed in water to prevent heating, since if the heat rises too high there is a secondary decomposition, and the product blackens very badly. At the same time the chloride of sulphur is volatilized before it can react on the hydrocarbon.



The figure shows the form of apparatus, found to be most convenient for this purpose.

By means of this the chloride of sulphur may be made to flow drop by drop, and the reaction



takes place in a gentle and regular manner.

When the reaction was finished, the mass was subjected to distillation by the aid of steam.

The first body to come over, was a light liquid, having a peculiar aromatic smell, boiling at  $161^{\circ}$ , and having an ~~an~~ index of refraction of 1.474, but whose rotary power was much less than that of turpentine. (Terpene)?

There was next obtained a slight amount of a white solid having the odor and general properties resembling those of camphor. Found to be turpentine chlorhydrate. Further than this we could not go, with steam, as there was no apparatus for superheating it.



The direct flame was then tried, but owing to the steam having condensed in the flask, the liquid "bumped," and finally broke the flask, the contents taking fire, and giving off, the familiar odor of burning rubber.

A fresh portion of the mixture was then distilled, using the direct flame from the beginning.

This worked very satisfactorily giving the same products as before.

The camphor like body was obtained in large quantities; and in addition a heavy dark red oil having the intensely fetid odor, peculiar to organic bodies containing sulphur. This oil continued to grow heavier and heavier as the heat increased. It finally left in the retort nothing but coke,

This dark red oil, partially decomposed on standing, growing turbid, and giving off fumes of sulphuretted hydrogen.

Another portion, <sup>was</sup> distilled in a partial vacuum, with the aid of a current of dry air. This reduced the temperature necessary to force the vapors out of the retort, and diminished the tendency to "cracking". With this apparatus all the products which could be distilled, were separated from the tarry residue, and were then subjected to fractional distillation.

For this purpose the bulb apparatus<sup>(1)</sup> was used. A thermometer was inserted at the top, to ascertain the temperature at which the vapors came over. The heat was regulated by means of an oil

---

(1) Fres. Zeitschrift, 1872, S. 207.



bath and thermometer.

In order to prevent "cracking", the pressure was reduced by means of the jet-aspirator,<sup>11</sup> and regulated by means of the apparatus shown below.

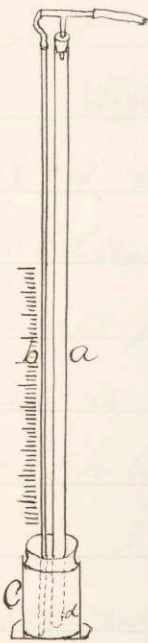
(a) is a glass tube about 15. m. m. in diameter, and 120 c. m. in length.

(b) is a finer tube, 4 or 5 m. m. in diameter and same length as (a).

(c) is a vessel containing mercury.

At (d) is a fine opening in the side of (a). When the apparatus is attached to the aspirator, the mercury rises in both tubes, until the level in (c) falls below (d) when air enters in fine stream, and bubbles thro' the mercury. A scale is

attached to the support back of (b), from which the pressure can be noted, as the mercury





in this tube is subject to scarcely any oscillation. The pressure may be increased or diminished by putting in or taking out mercury from the vessel (c).

With this form of apparatus, the separation was very much better, and the residue left in the retort was very small.

The pressure was first reduced to 334 m. m. The same products were obtained, as in the distillation at the normal pressure. The terebin(?) came over at a temperature of  $138^{\circ}$  and the turpentine chlorhydrate at  $160^{\circ}$ .

The pressure was now diminished to 100 m. m. Under this pressure the last portions of the turpentine chlorhydrate came over at  $138^{\circ}$  -  $145^{\circ}$ . The temperature now rose very rapidly to  $175^{\circ}$ , where it remained constant for a long time, finally rising to  $185^{\circ}$ . As this set of products seemed in every respect, similar

to those obtained by distillation at normal pressure, the two sets were mixed together and redistilled, fractioning every  $10^{\circ}$ , and these fractions were afterwards redistilled by themselves.

The whole finally separated into four principal bodies,

(1) Petroleum (?)

(2) Turpentine Chlorhydrate.

(3) A heavy yellow oil, having an exceedingly disagreeable odor, characteristic of sulpho-organic bodies.

(4) A solid tarry residue.

The consideration of (2), was done by Mr. Low, and will be found in his paper on the subject.

The consideration of (3), was by Mr. Wait, and will be found in the next section of this paper.

---

---



## Consideration of the Sulpho-Compound.

This body after being purified by repeated distillation was a heavy yellow oil, having an exceedingly fetid odor. It boils at  $168^{\circ}$  under a pressure of 100 m. m. and at  $248^{\circ}$  under the normal pressure, <sup>with slight decomposition,</sup> under the normal pressure. It is insoluble in water but mixes with alcohol, in all proportions.

Its sp. gr. at  $20^{\circ}$  is 1.0083. It is violently acted on by nitric acid, with the formation of a yellow body crystallizing in shining needles, and soluble in alcohol, and melting at  $182^{\circ}$ .

The writer attempted to make an analysis of this nitro-product, but it proved to be explosive, and he was obliged to give it up.

Two combustions of the sulpho-compound were made with chromate of lead



and oxide of copper, and the following are the results.

$$(1) \quad C = 72.54\% \quad H. = 7.41\%$$

$$(2) \quad C = 72.55 \quad H = 7.42$$

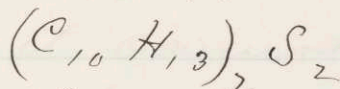
Next, an attempt was made to find the amount of sulphur in the body. The substance was heated for several hours, in a closed tube, with nitric acid of 1.2 sp. gr. at a temperature of  $180^{\circ}$ . At the end of this time the tube contained a considerable quantity of the crystalline nitro-compound spoken of before, which could not be broken up by further heating. This was then heated with strong nitric acid, (sp. gr. 1.4) and chlorate of potassium, and the sulphur determined as sulphate of barium.

The results were several per cent too low. Several other methods of decomposition were tried, e.g., heating in a closed tube with strong nitric acid, and bichromate of potassium;

suspending in hot solution of caustic soda, and oxidizing with chlorine; passing over red hot lime, and oxidizing with chlorine, etc. but all the results were too low. The best result was obtained by heating in closed tube, at  $150^{\circ}$ , with strong nitric acid and bichromate of potassium.

This result was  $S = 18.88\%$

The only bodies having a composition approaching these results are those having the formulas,



The first of which has never been prepared, hitherto.

We find as a comparison of the results of analysis, (after adding .06% to the carbon, and deducting .14% from the



hydrogen,) and the calculated compositions, the following,

	Found	$C_{10}H_{12}S$ .	$C_{10}H_{14}S$ .	$(C_{10}H_{13})_2S_2$
C	72.61%	73.18%	72.30%	72.74%
H	7.28	7.31	8.43	7.87
S	$\frac{18.88}{98.77}$	$\frac{19.51}{100.00}$	$\frac{19.27}{100.00}$	$\frac{19.39}{100.00}$

If the time had allowed another determination of sulphur, the writer has good reasons for supposing, that the result would have been at least .50% higher.

This would seem to point to the formula  $C_{10}H_{12}S$  as the true one.

That it cannot be either of the others may be proved conclusively.

The body  $C_{10}H_{14}S$  is described by Fleisch,<sup>11)</sup> as a colorless liquid, boiling at

---

11) Liebig and Kopp, Jahresbericht 1873, 433.



235°. Sp. gr. at 17°, 0.9975. It has a peculiar aromatic odor, somewhat resembling that of cymene, but has no similarity with the odor of most sulpho-organic bodies. This description shows that the two bodies cannot be identical.

That it cannot be the body  $(C_{10}H_{12})_2S_2$  is shown by the molecular weight which was determined as follows, by means of the molecular refractive energy.<sup>(1)</sup>

First the molecular refractive energy of sulphur was found, by determining the refractive energy of bisulphide of carbon.

At 16°C. the index of refraction, ( $n$ ) was 1.5929. and the density ( $d$ ) was 1.2715. From which we find

$$\frac{n-1}{d} = .4663 \text{ and } \rho\left(\frac{n-1}{d}\right) = 35.4$$

---

vide Publications of Landolt, and Gladstone.

Subtracting from this result, 5.2 the refractive energy of carbon, and we have  $S_2 = 30.4$  and  $S = 15.2$ .

The refractive energy of the body itself was next determined, at temperature  $20^\circ$

$$n = 1.5896 \text{ and } d = 1.0583$$

hence  $\frac{n-1}{d} = .5847$  and  $\rho \left( \frac{n-1}{d} \right) = 95.8$

The molecular refractive energy of turpentine was found to be  $77.8$ . Subtracting from this  $5.2$  the refractive energy of four atoms of hydrogen, and adding  $15.2$  the energy of sulphur, and we have the theoretical molecular refractive energy equal to  $87.8$ .

This would tend to prove that the atoms are more closely linked than in the terpene group, and it shows conclusively that the molecule is <sup>the</sup> single mol-



cell, and not the double one, as in the compound  $(C_{10}H_{13})_2S_2$ .

All this would seem to show that the body under consideration, might have the composition  $C_{10}H_{12}S$ , i.e., a sulpho-substitution product of cyrene.

However before anything definite can be proved with regard to its composition and molecular structure, it will be necessary to determine its reactions with other bodies. As the time allowed to students at the Institute, for researches of this character is necessarily very limited, it cannot be hoped that more than a beginning can be made by any one student. Still the slight results obtained thus far, would seem to uphold the theory advanced at the beginning of this paper, i.e., that vulcanization is a substitution of sulphur for hydrogen.



The writer hopes that at some time in the future, circumstances will permit him to carry the investigation, farther, and arrive at some definite conclusions on the subject, or if that be impossible, that what has been here written may induce some other investigator to carry on the research in the hopes of unravelling that curious and ~~with~~ incomprehensible mystery, vulgarization.

All of which is respectfully submitted,  
Charles Nelson Waite.