

PART I The Production of Carbon Black
and Activated Carbon from
Hydrocarbons and Chlorine

PART II Production and Pyrolysis of
Chlorinated n-Butanes

by

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I wish to express my sincere thanks to the Departments of Chemistry and of Mining and Metallurgy for the use of their equipment, to Dr. G. W. Stratton for the use of his laboratory and for his helpful suggestions, and to the other members of the Department of Chemistry who have helped me in this work.

PREFACE

This dissertation contains the results of work carried out in the Department of Chemistry at the University of Kansas. This work was made possible through a grant by the Kansas Legislature in 1939, and its purpose has been to find new uses for the natural resources of Kansas.

Since Kansas has an abundant supply of light hydrocarbons which are being wasted to a large extent at present, and since Kansas has a large potential supply of chlorine, this work has had as its object the utilization of these raw materials.

The combustion of hydrocarbons in chlorine as a method for obtaining carbon black, activated carbon, and HCl has met with some success. A carbon black of medium quality and an activated carbon of superior quality has been produced by methods easily adaptable to commercial production.

In another phase of this work, the chlorination of butane and the production and polymerization of butadiene and unsaturated chloro butanes, considerable information and a number of positive results have been obtained.

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Part I
Carbon Black

INTRODUCTION

The production of carbon black in the United States dates back to 1872¹. Before that time it was generally known as lampblack and was used as a pigment.

Carbon black was first added to rubber in 1915. Because of its unique reinforcing properties in rubber compositions, it has almost completely displaced zinc oxide as a filler in the rubber industry. In tire treads, proportions up to 45% of the rubber or 27 to 28% of the finished composition are added. Some realization of its importance in such uses may be gained from the statement that the incorporation of black increased the life of a tire from 5,000 to 20,000 miles. Besides its toughening characteristics, it appears to protect the rubber substance from the effects of light and may retard oxidation.¹

The production of carbon black in the United States for a six-year period is given in the following table.²

The figures represent thousands of pounds.

1930	1931	1932	1933	1934	1935
379,942	280,907	242,700	273,125	328,828	352,749

Used by rubber manufactures in the United States.

128,572	134,315	130,380	191,558	165,446	213,708
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Most of the remainder was exported or used in inks and paint.

At the present time there are five general methods for the production of carbon black which may be listed as follows:

1. Incomplete combustion with impingement.
2. Thermal decomposition.
3. Explosion with a limited supply of air.
4. Incomplete combustion without impingement.
5. Destructive distillation.

Most of the carbon black produced at the present time is made by the first method. The common name for this method is the channel process, and the product is called channel black. The carbon made by the second method is frequently referred to as thermatomic carbon. A common trade name for carbon made by the fourth method is Gastex.

Present yields by the channel process vary from 0.5 to 2 pounds of black per 1000 cu. ft. of natural gas, although 31.82 pounds of carbon are theoretically obtainable from 1000 cu. ft. of methane.³ It can readily be seen that this process is very wasteful and can be used only where gas is very cheap. Much work has been done in an attempt to increase yields by modifying the ratio of air to natural gas and by using different types of burners.

Much higher yields have been obtained by methods 2 and 4, but the carbons obtained have only limited use.

The use of chlorine and hydrocarbons as raw materials for producing carbon black and HCl, has never advanced past the laboratory stage. In the U. S. Patent Office there are four patents which describe the production of carbon black and HCl from chlorine and hydrocarbons. In 1917 Charles C. Averill⁴ described a method of producing carbon black and HCl by burning hydrocarbons in an atmosphere of chlorine. In 1918 William Roy Mott⁵ claimed that increased yields of carbon black could be obtained by the thermal decomposition of mixtures of methane and carbon tetrachloride. The carbon tetrachloride was obtained from methane and chlorine. Bradley W. Rumbarger in 1926⁶ claimed that increased yields of carbon could be obtained by first partially chlorinating the hydrocarbon and then burning in the usual manner in air. In 1924 John Ashfield McGuire⁷ reversed the process suggested by Averill and claimed that carbon black and HCl could be produced by burning chlorine in an atmosphere of hydrocarbons.

None of the above mentioned U. S. patents give any specifications for the carbon produced.

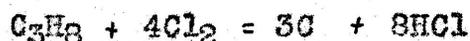
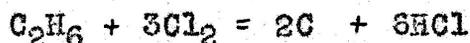
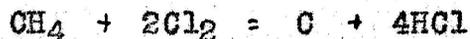
The following foreign patents claim the production of carbon and HCl from hydrocarbons and chlorine:

French 676,413;⁸ British 317,165,⁹ 343,676,¹⁰ and 343,477¹¹.

These foreign patents say the hydrocarbons and chlorine are burned in air.

THE PRODUCTION OF CARBON BLACK AT THE
UNIVERSITY OF KANSAS

The problem of producing carbon by the reaction between hydrocarbons and chlorine is much more difficult than one might at first suppose. The reactions;



seem rather simple but they don't explain all the possibilities. Methane for example has four different chlorinated derivatives. In addition, polymerizations may take place yielding any number of chlorinated products. At the temperatures ordinarily employed, natural gas is known to yield CCl_4 , C_2Cl_6 , high boiling chlorinated oils, tar, and a surprisingly large amount of hexachloro benzene.

Since the cost of the carbon produced is going to be determined largely by the cost of chlorine, it would be advantageous to use hydrocarbons in which the ratio of hydrogen atoms to carbon atoms is as small as possible. Among the gaseous hydrocarbons, butane immediately suggests itself. The gases, propylene and butylene from the cracking stills, also seem well suited for the process, but some probable disadvantages will be mentioned later.

At the start of this work, natural gas was used exclusively. Later, impure propane and butane were used. The products obtained depended more on the reaction con-

ditions and the ratio of hydrocarbon to chlorine than upon the type of hydrocarbon used.

The first type of burner used is shown in Figure I. This type of burner can be used in a number of different ways, and all ways that could be thought of were tried. The hydrocarbon may enter through the inner tube and the chlorine on the outside, or vice versa. The inner tube can be raised or lowered. The diameters of the two tubes may also be varied. Preheating the gases before mixing was tried along with the various other adjustments. Although considerable time and effort was spent on this type of burner, the results were not promising. Carbon has a tendency to bridge across the top of the burner and thus stop its operation. Frequently the burner goes out even though it is not clogged. Much tar and chlorinated derivatives are formed and hence the yield of carbon is low.

More elaborate burners with three or four small tubes equally spaced within one large tube gave better results but left much to be desired.

The above mentioned burners may be considered to represent conditions of a hydrocarbon burning in an atmosphere of chlorine or of chlorine burning in an atmosphere of hydrocarbons. These are the conditions mentioned in the patents of Averill⁴ and of McGuire⁷. An analysis of

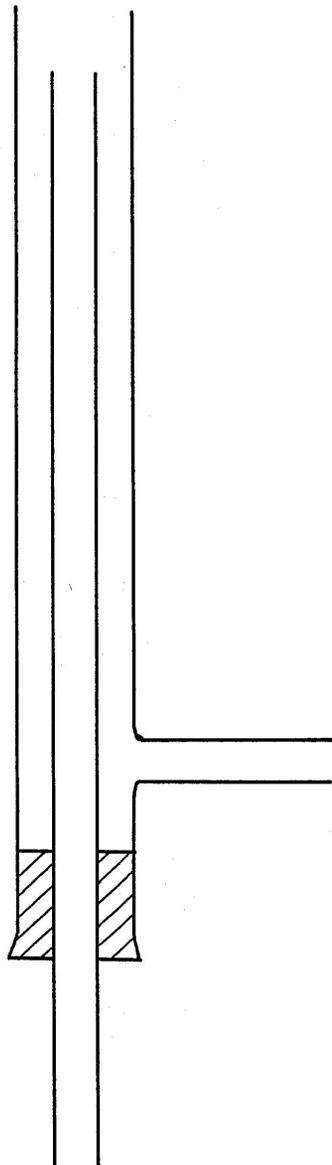


Fig I

the conditions which exist in such burners may be helpful in explaining the low yield of carbon and may point to better methods.

Since the two gases enter the reaction side by side and react immediately, there will be a difference in the concentrations of the two reaction gases at different parts of the flame, but there is only one ideal ratio of chlorine to hydrocarbon which will theoretically produce carbon and HCl. Either increasing or decreasing this ratio will tend to increase the formation of chlorinated derivatives. It seems logical that the best method to produce only carbon and HCl would involve thorough mixing of the chlorine and hydrocarbon before they react. Two different methods involving this principal of mixing before reacting have been used with considerable success and it is believed that either method could be used on a commercial scale.

The first of these methods to be discussed will be the one involving the explosion of proper mixtures of hydrocarbons and chlorine.

If any of the saturated hydrocarbon gases are mixed in a chamber with the theoretical amount of chlorine, as required for the production of carbon and HCl, and ignited, they will burn with explosive violence. A typical laboratory setup for carrying out this reaction is shown in

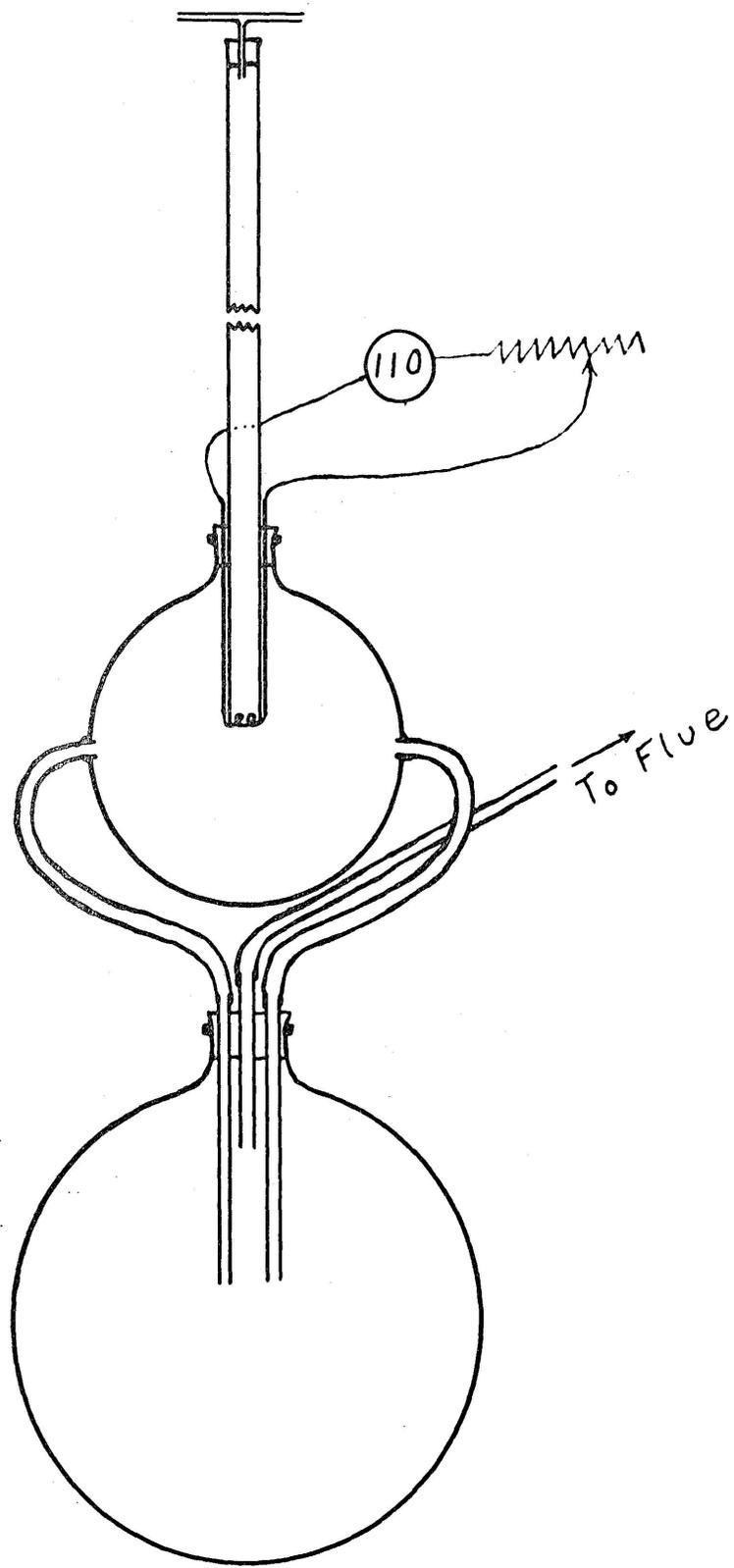


Fig II

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Figure II. The first expansion or settling chamber has a five liter capacity and the second a twelve liter capacity. The combustion tube must be selected in accordance with the size of the expansion chambers. For the apparatus described above, combustion tubes with an inside diameter of three to four centimeters and two to three feet long gave the best results. A tube with an inside diameter of 2.5 centimeters worked better with a three-foot length than with a five-foot length.

The gases enter one end of the combustion tube and are ignited at the other end by a hot nichrome wire. The flame spreads rapidly down the tube as a mixture of carbon and HCl gas issues from its mouth. When the explosion is complete, the combustion tube fills with another chlorine-hydrocarbon mixture. The products of combustion are pushed out, and when the new mixture reaches the hot wire, it is ignited. This process can go on continuously. One of the shortcomings of this process lies in the fact that the fresh gases as they enter the combustion tube will be mixed with considerable HCl and will not ignite when they reach the hot wire. If they do ignite, they burn rather feebly at first. Thus we have part of the gas either passing through unburned or reacting feebly and yielding a large percentage of chlorinated derivatives.

After each explosion, the entering gases have a tendency to catch fire and burn at the entrance. This can

be prevented by "pinching off" one of the gases for a second after each explosion. The problem of igniting the gases has been one of the most difficult to meet. A spark gap was first used, but this had a tendency to become shorted either at the base of the electrodes or directly across the electrodes. A nichrome wire heated just hot enough to ignite the gases serves very well as long as it lasts. (A 20 gauge nichrome wire will last for about six to eight hours of continuous service.)

Other modifications of the apparatus described above have been used but will not be described here since the principles involved are the same.

At the start of a run, the flow of gases must be adjusted to the proper proportions. This is done by passing the gases into a test combustion tube and exploding them into a hood. The ratio of chlorine to hydrocarbons is adjusted until their explosion yields the maximum amount of carbon as determined by observation of the cloud coming from the combustion tube. Best results are obtained when the gases enter the combustion tube at such a rate that an explosion occurs every fifteen to twenty seconds.

The following hydrocarbons have been burned by this method: natural gas, natural gas and acetylene, natural gas and benzene, natural gas and petroleum ether, propane, and butane.

Acetylene and chlorine cannot be mixed as they will ignite spontaneously. However, if acetylene is mixed with an equal volume of natural gas, it can then be mixed with chlorine and exploded. This mixture gave a more violent explosion than anything else tried, and the carbon produced contained fewer impurities than the carbon produced by other explosive mixtures. Propane-chlorine mixtures explode more violently than butane-chlorine mixtures and yield a more nearly pure carbon.

The first method used for the purification of carbon consisted in steam distillation followed by filtration, drying, and extraction with acetone in a Soxhlet extractor. Since the carbon as produced could not be wetted by water alone, some form of wetting agent had to be used. Soap or acetone added to the water served satisfactorily. Steam distillation generally yielded a small percentage of oil. The amount of oil generally increased with increase in molecular weight of the hydrocarbon used. The oil consisted of CCl_4 and other higher boiling chlorinated hydrocarbons. With continued steam distillation, crystals always collected on the condenser wall. These crystals have been removed, recrystallized from Skelly Solve, and identified as hexachloro benzene.

	Found	C_6H_6
Molecular weight	280-299	285
Chlorine	73.3%	74.7%
Melting point	223	224-26

It is believed that hexachloro benzene makes up from 30% to 50% of the chlorinated products in the carbon. No accurate checks have been made on this belief because of the difficulty involved in separating the C_6Cl_6 from the carbon and other Cl derivatives--extraction yields a deeply colored solution; much of the C_6Cl_6 is decomposed if driven off as a vapor. Sublimation methods would probably give the best results. If the impure carbon is heated several hours on a sand bath at 110° , the surface becomes covered with long white needles of C_6Cl_6 .

Acetone extraction of the carbon which has been steam distilled and dried is carried out as follows: About five or six grams of dried carbon are placed in a paper thimble in a Soxhlet extractor and extracted with acetone until the solution comes through practically clear. This requires about three hours. The acetone in the receiving flask is evaporated and the gain in weight of the flask is taken as the weight of the chlorinated substances.

The acetone extractions of carbons produced by explosive methods generally lie between 22% to 40%, with extractions above 70% having been obtained from carbon produced with a large excess of chlorine.

The acetone extraction of a carbon, while used as a method for the evaluation of carbons, is not altogether reliable¹². It would take days for the extraction to be-

come complete, and it is difficult to prevent carbon from passing through the extraction thimble. Carbon which has been extracted as described may still contain from 10% to 15% chlorine by analysis. From what has just been said, we can see that the carbon as produced by explosive methods may contain from 30% to 50% by weight of chlorinated derivatives. This would, however, represent a yield of carbon of 85% to 90% based upon hydrocarbons consumed.

Since this carbon was being produced with the hope that it could be used in the rubber industry, it was necessary to make it meet the requirements of the rubber industry as nearly as possible. Some of the requirements of the Goodyear Tire and Rubber Company are as follows:¹³

Through 325 mesh	99.90%
Grit	none
Ash (maximum)	0.10%
Acetone extract (maximum)	0.50%

The particle size of carbon black should be in the neighborhood of 50 millimicrons.¹⁴ Some idea of particle size can be obtained from tinting strength¹² and from rate of settling,¹⁵ but these methods are not too reliable and are seldom used by rubber companies at the present time. Compounding tests with rubber are the final and deciding tests as to whether or not the material is satisfactory.

Some measurements on the settling rate of our carbon compared with Huber's channel black have been made. The carbon used in these tests had not been purified. Light suspensions of the two carbons were obtained by shaking in Skelly Solve to which a few drops of oleic acid had been added. Ten ml. of each of the suspensions were placed into two standard cells, and the rate of settling past a given level was determined by measuring ~~and~~ the percent of light transmitted by each solution. A Coleman spectrophotometer was used in making these measurements. Typical data are given in the following table:

Percent of Light Transmitted
Pure Skelly Solve = 100

<u>Time</u> <u>Minutes</u>	<u>K.U. Carbon</u>	<u>Channel Black</u>
0	28.8	32.1
10	30.4	42.0
20	31.6	50.9
30	33.1	56.4
40	34.0	59.8
50	35.3	62.8
70	38.0	71.0
90	39.2	75.7
110	41.0	78.2
155	46.2	86.0
210	49.8	89.4
270	53.0	91.6
330	55.8	92.9
390	57.8	93.8

Table I

These tests indicate that the K. U. carbon was composed of smaller particles because it settled more slowly. It must be pointed out that this test is not too reliable because it is difficult to disperse a carbon into its actual particles.

It is quite evident that our carbon must be purified by some method. An extraction method of purifying would probably prove rather expensive due to the large amount of solvent required and due to the difficulty of filtering the very fine carbon particles from the solvent. Heating the carbon in the absence of air seemed to offer possibilities as a method for purification. It was found that a black with an acetone extract of around 0.5% could be prepared by heating a sample of carbon in an Erlenmeyer flask over bunsen burners and with occasional stirring until no more fumes were noticeable. If the carbon black was first wetted with water, filtered, and dried, it occupied a smaller volume and more could be heated at one time.

Around 240 g. of carbon black--prepared by the explosive method and purified by wetting, drying, and heating in Erlenmeyer flasks, followed by washing with water; drying, and sifting through a 40 mesh sieve--were sent to the Firestone Tire and Rubber Company and compounded with rubber stock. The following is the report as given by Mr. J. N. Street of the Firestone Tire and Rubber Company:

When you were in Akron two or three weeks ago, you left with us two samples of black, designating one as purified and the other untreated. In view of the small amount of untreated material, we have not attempted to get anything on this so far.

Preliminary results with the treated sample are now available. The sample was compounded in a standard carbon black formula, similar to a tire tread formula, substituting your material on a weight-for-weight basis, for the channel process black normally contained. Results are as follows:

Cured @ 274° F.	Stress @ 400% Elongation					
	30'	50'	70'	90'	110'	130'
Channel	1625	2000	2125	2175	2250	2250
Exper.	1075	2225	2675	-----	-----	-----

Cured @ 274° F.	Tensile Strength @ Break					
	30'	50'	70'	90'	110'	130'
Channel	3375	3925	3900	3900	3800	3800
Exper.	1175	2275	2775	2850	3000	2825

Cured @ 274° F.	% Elongation @ Break				
	30'	50'	70'	90'	110'
Channel	595	595	580	580	560
Exper.	420	405	390	380	370

Under "Stress @ 400% Elongation", you will note that the experimental black at the longer times of cure

has given higher values, or, in other words, is a stiffer stock. This characteristic is parallel to that of reinforcing blacks of somewhat larger particle size, such as Gastex. It is not a particularly desirable property although it may not be serious. Tensile strength of the experimental sample is very definitely low; elongation at break is also low. The conclusion is, consequently, that in its present form this particular sample of black does not lend itself to direct substitution for channel black for use in rubber.

We would point out, however, as indicated in our talk with you here, that with a new pigment of this kind, the effect in rubber may be dependent to a very considerable extent on the "compounding" of the rubber stock. In other words, it might be possible to work out a much better combination whereby more satisfactory properties could be obtained. In order to carry out such work it would be necessary to have an appreciable amount of material.

From this one test we are not sure that we can give you too many thoughts regarding why these results were obtained. Were the difficulty one of particle size, we would expect to get a higher tensile strength than we have obtained, particularly with the 400% stress as high as it is. This then would point more to the surface character-

istics of the black as being responsible for the low tensile strengths produced. It would probably be easier to establish this from compounding in rubber, testing the effect of compounding changes before attempting to alter the preparation of the black.

The direction in which to turn was not entirely clear, so a larger sample, around 500 g., was prepared and sent to the Goodyear Tire and Rubber Company to be tested by compounding with rubber.

Since the presence of some metals in carbon black is very injurious when used in rubber, the carbon sent to Goodyear was prepared in the absence of all metal except the small nichrome wire used for igniting the gases. (Some of the carbon sent to Firestone had been prepared in an iron barrel.) The method of purification differed in that the carbon was not wetted before heating, and the heating was carried out in a furnace, the carbon being placed inside a two-gallon earthenware jar. The temperature of the furnace was around 600° C. and the heating was continued for around four hours. A carbon with an acetone extract slightly above 1% was obtained. As a final treatment, the carbon was washed with water, dried, and sifted through a 40 mesh sieve.

This black had a DPG number around 400 to 450. It was known that this value was high compared to the DPG number of Huber's channel black of 130 as found in this laboratory. The DPG (diphenyl guanidine) number or accelerator adsorption test is supposed to be an index to the rate of curing of the black. The higher the DPG number, the slower curing is the black. The method used for determining this number is similar to that used in the Huber Laboratories.¹⁶ Two grams of black are shaken off and on over a period of twenty minutes with 100 ml. of 0.01 N DPG solution. The solution is filtered and 10 ml. portions are titrated with 0.01 N HCl, methyl red being used as an indicator. A blank should always be run. The DPG number is taken as the number of grams of accelerator adsorbed by 10,000 grams of black.

The following report was received from Mr. E. Cousins of the Goodyear Tire & Rubber Company:

We have examined the black which you sent us and are glad to comply with your request that we give you our findings on this material as a compounding ingredient for rubber. Our analysis of the black in comparison with an ordinary rubber black is:

	Your black	Standard rubber gas black
Ash	0.10%	0.1%
Acetone extract	1.30%	0.5% (max.)
pH	3.33	4.0
DPG Adsorption	78.7%	38%
Water extract	1.82%	none
Chlorides in W.E.	0.41%	none
Total Chlorides	10.08%	none

Microscopical examination shows that the particle size of your black is greater than that of standard gas black. However, it is much finer than the thermal decomposition blacks, such as Thermatomic. The uniformity of particle size is fairly good.

To study the effect of this black in rubber compounding, we have tried, in a compound accelerated with mercaptobenzothiazole and containing about 50% by weight of the black on the rubber. This was compared with a stock containing an equal amount of standard gas black.

The results follow:

<u>Cure</u> <u>Min @ 260</u>	<u>Tensile</u> <u>Kg/cm²</u>	<u>Elong</u> <u>%</u>	<u>State of</u> <u>Cure</u>	<u>Load at 300%</u> <u>Kg/cm²</u>	<u>500%</u> <u>Kg/cm²</u>
<u>R-103D-43 Standard Gas Black</u>					
35	192	690	undercured	38	104
50	261	680	slightly under	63	153
70	296	655	good cure	78	190
100	305	630	overcured	97	215
140	312	605	overcured	108	235

On the Goodyear Flexing Machine this stock ran 126 min.

On the Goodyear Abrasion Machine the loss was 9.88 cc.

On the DuPont Abrasion Machine the loss was 301 cc/HP Hr.

R-103D-45 Your Black

<u>Cure</u>	<u>Tensile</u>	<u>Elong.</u>	<u>State</u>	<u>Load at 300%</u>	<u>500%</u>
35	36	415	undercured	24	
50	52	340	undercured	45	
70	76	330	slightly under	68	
100	93	285	good cure		
140	107	275	slightly over		

On the Goodgear Flexing machine this stock ran 27 min.

On the Abrasion machine tests the stock wore down rapidly and became gummy. Because of this adhering material, the loss could not be determined. However, it is high.

Upon examination, the stock made with this latter black is found to be weaker and much less lively.

In milling the black into the rubber in the laboratory, it was found that the black tended to float off in the air very much more than does standard black. The loss thru this effect was 12%, about ten times as much as for the standard. It was also found very difficult to mill your black into the rubber, taking about six times as long as for the standard black. Both of these features are important from the viewpoint of using the black commercially.

Analyzing the test results, you will note that the stock having your black is somewhat slower in vulcanizing, that the tensile strength is much less, and that the elongations obtainable before break are also much less. Also that the resistance of this stock to flexing and to abrasion is much less. All of these properties are important in

determining the ability of a rubber compound to give satisfactory service.

The nature of the results also indicate that your black would not satisfactorily replace such blacks as Thermatomic. Blacks such as these give comparatively high elongations at break.

We believe that, with your black, the matter of particle size could be adjusted thru manipulation of the burning process. The tendency of the black to fly off might also be modified without great difficulty. Modification of the process to reduce the amount of chlorine in the black and the elimination of free HCl, should offer promising avenues of approach toward obtaining a more satisfactory black.

We hope the above information will be of value to you. We shall be glad to elaborate this information in any respect you may desire, if possible, and we shall also be glad to try to answer any questions you may have.

Your process and results obtained are quite interesting and we shall be pleased to hear of your progress and to cooperate in evaluating future samples.

After examining the two forgoing reports it is clearly evident that such carbon cannot compete with channel black in the rubber industry. A brief discussion

of what might be wrong according to our opinions will now be made. The particle size of a carbon is one of its most important characteristics insofar as its use in rubber is concerned. The two reports mention that the particle size of our carbon may be larger than that of channel black, but this isn't stated definitely. The small difference in particle size could not account for the results obtained. Whether or not it is possible to alter the particle size of our carbon by altering the method of preparation is not known. We believe the trouble lies elsewhere.

The DPG number of our carbon is high. This means that it has a slower rate of curing. This may not be a serious fault other than that it would add to the cost of processing the rubber. However, methods have been developed for controlling the DPG number of the black so this variable is under control.

As to dusting, we know that our black has a very low apparent specific gravity and, therefore, floats away in the air easily. Goodyear mentions that this could probably be overcome. The manufacturers of channel black have met this problem by converting their carbon into pellets. These pellets are tiny balls of carbon which are not dusty, pour readily, and greatly decrease the

volume occupied by a unit weight of carbon. The actual process used for pelleting the carbon is patented and not much is known about it, but it is believed that our carbon could be subjected to the same treatment. Methods of pelleting the black as described in the literature^{17, 18} involve shaking a suspension of the carbon with two immiscible liquids, separating and drying. Considerable work has been done along this line but the results obtained in this laboratory have been negative.

Mr. Street of Firestone suggested that the low tensile strength of our carbon in rubber may be due to some surface characteristics of the carbon. Mr. Cousins of Goodyear stated that it was difficult to mill our carbon into the rubber, which also indicates a fault in the surface characteristics of the carbon. One of the theories of the increase in tensile strength of rubber on the addition of carbon black is that the attractive force between rubber molecules and carbon black is greater than the attractive force between two rubber molecules. If this theory is true, we can readily understand how the surface characteristics of a carbon would be an important factor. Mr. G. R. Johnson¹⁹ of the Godfrey L. Cabot Laboratories states that increases in volatile matter on a carbon decreases tensile at break.

We believe that the poor results obtained from the sample of black sent to Goodyear can be attributed largely to its high chlorine content, most of the chlorine being present as chlorine derivatives of hydrocarbons. Since we were relying on the acetone extract as a method for determining the purity of the carbon, no analysis for chlorine was ever run on the first sample of carbon sent to Firestone. However, since the carbon sent to Firestone was purified at a higher temperature and since it did have a much lower acetone extraction value, we have reason to believe that it was much purer. The results obtained from Goodyear, therefore, indicate that chlorinated derivatives are harmful and must be removed.

The next task undertaken was the production of another sample of carbon black. Before preparing this sample, a new method for the production of carbon and a new method for purification was developed.

Since the explosive method required constant attention due to the fact that the entering gases had a strong tendency to ignite after each explosion, and since the product obtained by this method contained a rather high percentage of chlorinated derivatives, it was hoped that a new method could be developed which would require less attention, would be easier to control, and would yield a more nearly pure carbon.

Burners of the Bunsen and Meker burner types in which chlorine was burned in an atmosphere of hydrocarbons or vice versa were tried but were unsuccessful due to the fact that the flame would always strike back. A torch type burner as shown in Figure III was developed after much experimentation and has proven to be quite successful. The chlorine and hydrocarbon gases first come into contact with each other at the bottom of the burner, they become thoroughly mixed on their way up, and are burned at the mouth of the burner. The arrangement at the bottom of the burner serves as a reservoir to collect the small amount of liquid chlorinated hydrocarbons formed inside the burner tube. It is very essential to the best operation of the burner that the diameter of the inside tube be slightly smaller at the mouth than at the rest of its length. This has a tendency to prevent the flame from striking back and also retards the formation of a ring of carbon around the mouth of the burner on the inside. The burner must be cooled; otherwise, it becomes too hot. If the tube becomes hot, it acts as a catalyst for the reaction and the burning soon takes place down inside the tube and the tube soon becomes clogged with carbon. The velocity of the gas through the burner must lie between definite limits which can be determined from experience. If the velocity is too low, the flame will travel down the tube. If the velocity is

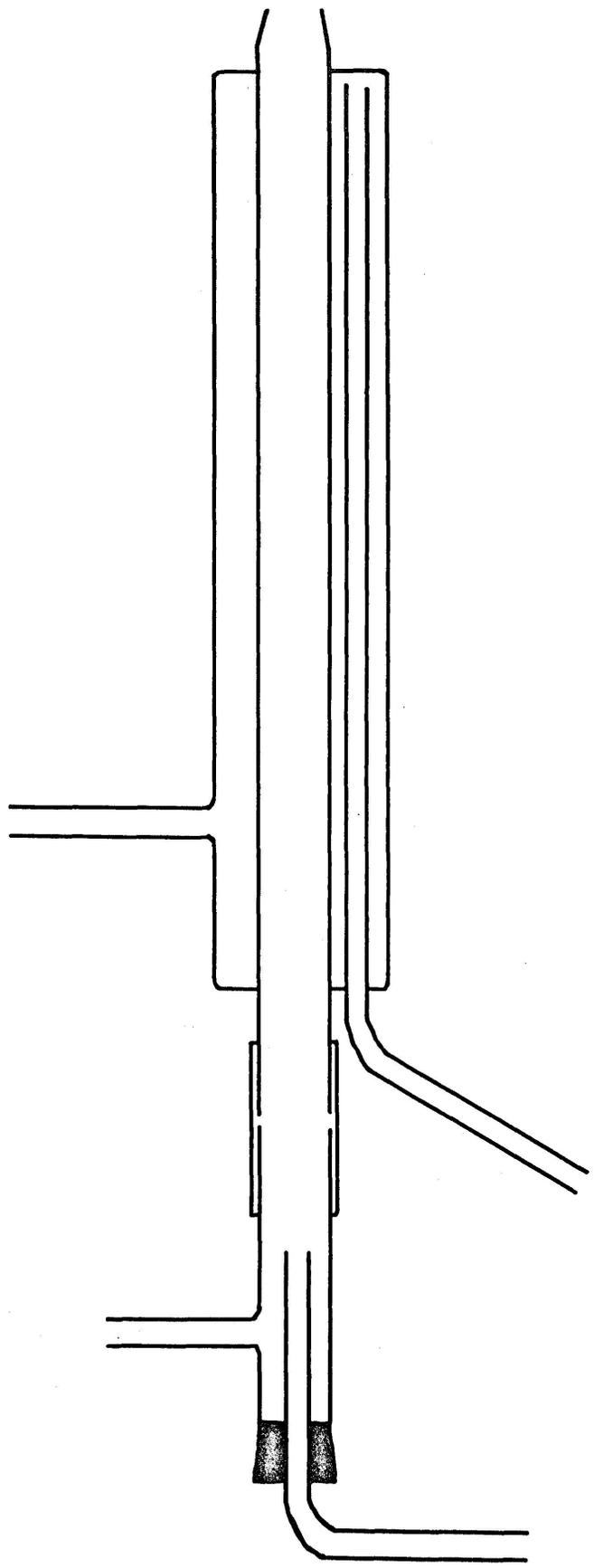


Fig III

too great, the flame will be blown out. To determine if the proper mixture of chlorine and hydrocarbons is being used, one need only look at the amount of smoke being formed and adjust the ratio until the smoke is very black and copious and flakes of soot are seen floating in the cloud. If chlorine is in excess, the cloud becomes thin and light in color, almost white. If hydrocarbon is in excess, the cloud becomes less dense, lighter in color, and no flakes of soot are noticeable. With a little experience one can tell if the proper mixture is being used by looking at the cone in the flame. If the mixture is correct, the cone will be intensely colored and very sharp. With an excess of either of the gases the cone becomes larger, it isn't very sharp, and its color becomes dull.

The chief fault of this burner lies in the fact that it has a tendency to build carbon formations at its mouth. These formations grow until they build across the mouth or until a chunk falls down inside and the flame strikes back. Best results are obtained if the flame is not under any pressure other than atmospheric, and the products of combustion are free to move away as rapidly as produced. Mechanical methods for cleaning the burner while in use disturb the flame and increase its tendency to strike back.

The two hydrocarbons which have been most extensively used in this burner are commercial propane and butane. Propane has a greater tendency than butane to strike back. This is probably an indication that propane is more reactive than butane. The unsaturated gases as propylene and butylene are still more reactive, and it is believed that one might experience more difficulty in burning these gases in a torch type burner.

The carbon produced by this new burner has a much lower acetone extract than the carbon produced by explosive methods -- from 10 to 20% compared to 22 to 40%.

The actual amount of volatile constituents present in the carbon produced by a torch type burner has been determined for two samples of carbon made on two different days. The carbon was wetted with Skelly Solve to decrease its volume, dried in air over night, and then at 110° for thirty minutes. The carbon was weighed into #1 porcela in crucibles with lids and heated fifteen minutes over a Meker burner. The loss in weight was taken to represent volatile matter. The results obtained were 25.7% and 27.5%. On the basis of 26% volatile material, and assuming this to be C_6Cl_6 , we would have approximately a 92% yield of carbon. This, of course, assumes that all carbon compounds used as hydrocarbons enter into some reaction

and form either carbon or slightly volatile chloro carbon compounds. Experience indicates that this assumption is permissible.

The new method used in the purification of the carbon in preparation for its compounding tests in rubber was similar to the other methods previously described, but the conditions of heating were different and the temperature was more closely controlled. The criterion for purity was not acetone extraction but, rather, analysis for chlorine.

It was known that all the chlorine could be removed from a sample of carbon by heating to a sufficiently high temperature. It was also known that heating a carbon increased its DPG number. This latter fact was very undesirable if the carbon was to be used with rubber.

In order to work out a method to purify the carbon and at the same time keep the DPG number low, the following experiments were carried out. Samples of carbon were heated under the following conditions:

1. Heated in a covered clay crucible 45 min. at 500° C.
2. " " " " " " " " " 600° C.
3. " " " " " " " " " 700° C.
4. Heated in a current of natural gas 35 min. at 500° C.
5. " " " " " " " " " 600° C.
6. " " " " " steam 30 min. at 400° C.

7. Heated in a current of steam 10 min. at 600° C.
 8. " " " " " natural gas 35 min. at 600° C.

Table II

In all the above trials, the moist carbon and its containing vessels were placed in a cold furnace. The temperature was allowed to rise until the desired conditions were attained, and then held constant for the stated period of time. In the first three trials, the carbon was heated in a covered vessel. In the next five the carbon was inside a pyrex tube (20 mm. inside diameter). The gases passed over the carbon were preheated to the temperature of the furnace by passing through four feet of 9 mm. tubing. The natural gas passed through at the rate of 2 to 3 cc. per second, the steam at a somewhat higher rate. In trial (8) the natural gas continued to flow over the carbon while cooling to 200°.

The adsorptive capacities of these carbons along with the percent chlorine, as determined by fusion with sodium peroxide, are given in the following table:

Trial	Iodine number	% Cl
1	631	3.4
2	672	0.2
3	741	0.0
4	448	1.5
5	447	0.0

Trial	Iodine number	% Cl
6	384	6.5
7	664	0.2
8	415	0.0

Table III

The iodine number as given above represents the number of grams of iodine adsorbed by 1000 grams of carbon black. It is determined by adding 100 ml. 0.1 N iodine solution to 1 gram of carbon black in an Erlenmeyer flask, shaking occasionally for twenty minutes, filtering and titrating 10 ml. portions of the filtrate with standard sodium thiosulfate solution. The iodine number rather than the DPG number was used in these tests because it is much easier to determine and there is a direct correlation between iodine number and DPG number.

The above data indicates that a carbon purified as in trial (8) should be most suitable for use in rubber. It is free from chlorine derivatives. It has a DPG number of 177 which is higher than the DPG number of Huber's channel black as determined in this laboratory, but is much lower than the DPG number of the black sent to Good-year. A carbon-hydrogen analysis indicates that the adsorbed natural gas cannot exceed 3% which is not a serious matter.

About 570 g. of carbon black prepared by the burner method and purified by a method similar to trial (8) were sent to the Firestone Tire and Rubber Company to be compounded in rubber and tested. This black was prepared entirely with glass equipment--even glass burners were used. To purify the black, it was first wetted with water to reduce its volume. (Drene soap was used as a wetting agent to guard against contamination by a metallic ion.) It was then placed inside 45 mm. pyrex tubes and heated one hour at 600° C. with natural gas passing over it during the heating and while cooling. The black was then sifted through a thirty-mesh sieve. The average chlorine content of the batches prepared in the above manner was around 0.5% and the DPG number was around 190.

The following report on this carbon black was received from Mr. J. N. Street of the Firestone Tire and Rubber Company:

Tests on your sample of carbon black, in comparison to regular rubber channel black, were as follows:

Cured @ 274° F	Stress @ 400% Elongation						
	15'	30'	50'	70'	90'	110'	130'
Channel	1050	1675	2300	2425	2425	2525	2625
Exper.	1500	----	2900	3125	----	3200	3275

<u>Cured @</u> <u>274° F</u>	<u>Tensile Strength @ Break</u>						
	<u>15'</u>	<u>30'</u>	<u>50'</u>	<u>70'</u>	<u>90'</u>	<u>110'</u>	<u>130'</u>
Channel	2450	3500	3850	4050	3825	3850	3800
Exper.	1575	2000	3000	3250	2800	3050	3125

<u>Cured @</u> <u>274° F</u>	<u>Elongation Strength @ Break</u>						
	<u>15'</u>	<u>30'</u>	<u>50'</u>	<u>70'</u>	<u>90'</u>	<u>110'</u>	<u>130'</u>
Channel	650	625	570	570	545	540	525
Exper.	410	375	410	415	365	400	400

The above tests would indicate that the experimental black is not acceptable as a replacement for the present type of channel black. However, it has been noted that your material has a very appreciable amount of grit, compared to the standard product. This will probably cause a lowering of both tensile and elongation. To what extent the lower tensile and elongation are due to this, we do not know.

We find your pH, DPG adsorption, volatile matter, and moisture content in a range which is not excessively far from that of our normal channel blacks. The main difference is that DPG adsorption is quite low, which ordinarily would indicate a fast curing black. This is probably offset by either chlorine content or mode of preparation. Higher modulus as well as low DPG adsorption might be indicative of somewhat larger particle size. This again may be incorrect, however, in view of the dif-

ference of preparation involved. We have not made particle size measurement.

If the above report from the second batch of carbon black sent to Firestone is compared with the first report from the same laboratories, we note the following: The stress at 400% elongation is higher, indicating a stiffer black. Tensile strength at break is much higher at the low curing times and about the same at the high curing times. The percent elongation at break is slightly higher.

Mr. Street says the DPG number is low. We thought it was slightly high. However, that property can be easily altered by changing the temperature of purification.

We know that our carbon has a tendency to become gritty when purified by heating, but we thought the grits would be mashed on the calender rolls when the carbon was being worked into the rubber. Evidently they were not mashed completely. The presence of grit might explain the low tensile at break and the low percent elongation at break. The two blanks under stress at 400% elongation could easily be due to the presence of grit in the test piece which caused it to break before 400% elongation.

The grit in our carbon could easily be ground and this would no doubt increase its value to the rubber, but just how much we would be afraid to say. A modification

in the method of purification may prevent the formation of grit. We would suggest stirring the carbon while it is being heated. This would add to the difficulties encountered on a laboratory scale, but may not be a serious disadvantage on a commercial scale.

It should be pointed out that in all tests made on our carbon by the rubber companies, our carbon was compared with channel black and the compounding formula used was the formula developed after years of research, especially for channel black. Since our carbon black is entirely new insofar as its actual use in rubber is concerned, it is quite possible that much better results could be obtained from it if different methods of compounding were tried. If any future work is carried out in this field, more thought should be given to methods of compounding.

CONCLUSION

Two methods for the production of carbon from hydrocarbons and chlorine have been developed. It is believed that these methods are sufficiently different from other methods described to be considered new. This carbon can be purified by heating. In its present state of development, this carbon cannot replace channel black as a reinforcing filler in rubber.

Part II
Activated Carbon

INTRODUCTION

As far back as 1777, Scheele and Fontana discovered that wood charcoal would adsorb gases and a few years later Lowitz recorded that colored liquids could be decolorized by filtration through the same medium. However, only limited practical use was made of these discoveries, probably due to the large quantities of wood charcoal required. In 1810 Figuier proved that bone charcoal possessed considerably more adsorbent properties than ordinary wood charcoal, and in 1822 Payen described a method of decolorizing beet sugar with bone char which later came into general use for the decolorizing of sugar juices.²⁰

During the early years of the 20th century research laboratories throughout the world studied methods of making a more active charcoal. The use of gas in the world war provided a great stimulus to both research and manufacture in this field, and made the world active carbon conscious.

A definition of activated carbon is taken from the "Condensed Chemical Dictionary," Second Edition (Turner).

Activated Charcoal (Active carbon). A more or less pure form of carbon characterized by a high adsorptive capacity for foreign molecules. This adsorptive power is due partly to the chemical nature of the carbon atom with its attendant free valences and partly to the capillary structure of the charcoal, which presents an enormous adsorptive surface. Other factors, such as condensation of gases and vapors in the capillaries, solid solution and chemical combination, also contribute to its adsorptive power. Activated charcoals cover a wide range of adsorptive power for various foreign molecules, depending primarily upon the size and chemical properties of the molecules to be adsorbed.

In the manufacture of activated carbon, various raw materials are utilized, generally of vegetable origin. Production is usually carried on under patented processes, making use of gases, such as air, steam, carbon dioxide, chlorine, and similar materials, involving treatment at high temperatures. In some instances the carbon is impregnated with phosphoric or sulfuric acid, zinc chloride, or various other salts, followed by heating to a high temperature. In the processing, a porosity is obtained that has an important bearing upon the ultimate efficiency of the product.

Activated carbon is finding wide uses at the present time. Probably its two most important uses are in the purification of water and in the refining of all kinds of sugar. Other products which are frequently refined with activated carbon are: oils, fats, glycerine, gelatine, fruit juices, vinegar, whisky, wine, numerous chemicals and pharmaceuticals, and used dry cleaning solutions.

THE PRODUCTION OF ACTIVATED CARBON AT

THE UNIVERSITY OF KANSAS

From the studies made on the purification of our carbon black it was noticed that continued heating or heating at a higher temperature had a tendency to increase the DPG number of the carbon, or in other words to make it more active.

Since a good activated carbon will sell for from two to three times as much as channel black, it was considered advisable to investigate the possibilities which our carbon might possess as an activated carbon.

The mode of preparation of this carbon has been described in the first part of this thesis under production of carbon black. The subsequent treatment of the impure carbon after formation determines whether or not it will be an activated carbon. All activated carbon produced in this laboratory has been made from carbon produced by the torch burner method.

The first indication that our carbon could be activated was obtained, as has just been mentioned, when it was found that the DPG number could be varied within wide limits by different heat treatments.

In order to determine the heat treatment which would produce the best activated carbon, a number of trials were run under different conditions. In the first five trials, the dry carbon was packed into fire clay crucibles provided with covers and the heating was carried out in a

muffle furnace. (The fire clay crucibles mentioned in this work are four inches high and their inside diameter at their top is three inches). In the sixth trial the dry carbon was placed in a somewhat larger graphite crucible and heated by a direct flame in a small furnace. In all cases the carbon was placed in a cold furnace, heated to the approximate temperature indicated, and then held at that temperature for the specified time. When the time indicated had elapsed, the crucibles were withdrawn and allowed to cool. Before running tests on the carbon it was sifted through a 30 mesh sieve. The heat treatments for the various trials were as follows:

1. Heated 45 minutes at 600° C.
2. " " " " " " then 30 minutes at 700° C.
3. " " " " " 800° C.
4. " " " " " 950° C.
5. " 90 " " " 950° C.
6. " 20 " " " 500° C. then 30 min. at 1100° C.

In the following table carbons 7, 8, 9, and 10 are activated carbons used for comparison. All were dried one hour at 110° C. Number 7 is the well known Norit, 8 is a carbon used by the city of Lawrence for water purification, and 9 and 10 are two activated carbons put out by two different companies and are supposed to be of superior quality.

Adsorption data was obtained for three different

solutions, one at two concentrations. Under iodine number are given values whose significance has already been explained. Under iodine number on 0.2 N solution, a 0.2 N instead of a 0.1 N iodine solution was used. The rest of the procedure was the same. (All future references to iodine numbers will be values obtained on 0.1 N iodine-KI solutions made as previously described). The DPG numbers given in this table were determined, using a modification of the method previously given, that is, 1 g. of carbon instead of 2 g. was treated with 100 ml. of 0.01 N DPG solution. Under benzoic acid number are given the grams benzoic acid adsorbed by 1000 g. activated carbon. The determination was run as follows: A 0.05 N benzoic acid solution was prepared in a solvent containing four volumes of ethyl alcohol to six volumes of water. 100 ml. of this solution at room temperature was shaken occasionally over a twenty-minute period with 1 g. of activated carbon. The solution was then filtered and 10 ml. portions were titrated with standard NaOH using phenolphthalein as an indicator. Results are given in the following table:

Sample	Iodine number	Iodine number on 0.2 N solution	DPG number	Benzoic acid number
1	631			
2	672			
3	741	805	1004	217
4	958	1075	1418	295
5	1004	1204	1421	327
6	897	980	918	264
7	836	904	687	247
8	610	648	258	162
9	845		1790	251
10	1000		1125	298

Table IV

These results indicated that our carbon definitely had possibilities as an activated carbon.

Upon analysis of the above results it seems that temperature plays a very important role in the activation of our carbon. It appears that temperatures around 950° C. are best and that temperatures around 1100° C. are too high. There is probably a change in the structure of the carbon at this high temperature. The duration of the heat treatment at 950° had little effect on the DPG number, increased the benzoic acid number 10% and increased the iodine numbers 5% to 10%.

Since carbon conducts heat rather slowly, it was considered advisable to determine the time required for

the carbon in the center of the crucible to become heated to the same temperature as the furnace. To do this, a thermocouple was placed in the center of a fire-clay crucible packed with dry carbon and the crucible was placed in a gas bath at around 660° C. The following data was taken:

Time elapsed in minutes	Temperature of thermocouple
10	127
20	300
25	445
30	552
40	642
50	657
60	657

Table V

This data indicates that it would take from 45 to 60 minutes for all the carbon in a crucible to reach its maximum temperature if placed in a hot furnace at 950° C.

The carbons in Table IV had been placed into a cold furnace and were allowed to heat up with the furnace. It takes the furnace a little more than an hour to reach a temperature of 950° C., so it seems reasonable to assume that the temperature of the carbon is not far behind the furnace temperature.

In order to get a further check on the effects of

time and temperature on activation, another series of experiments were run. This time we wanted to heat the carbon as rapidly as possible to a certain temperature, hold it at this temperature for a definite length of time, and then cool it in the air. Number one porcelain crucibles were used. In order to increase the amount of carbon which could be heated in a single crucible, it was first wetted with Skelly Solve and then dried before being placed into the crucibles. In all trials but one, the crucibles were placed in direct contact with a flame of the desired temperature. In the other case the crucibles were placed into an electric furnace of the desired temperature. In all cases the contents of the crucibles should have been heated to the desired temperature in a few minutes. After heating, the crucibles were allowed to cool, the carbon was ground and screened through a 40 mesh screen, and the iodine number determined. The following results were obtained:

<u>Temperature</u>	<u>Minutes</u>	<u>Iodine number</u>
850	30	683
"	60	773
<u>"</u>	<u>90</u>	<u>785</u>
960	30	735
"	60	723
<u>"</u>	<u>90</u>	<u>930</u>
1050	25	719

1050	50	885
<u> "</u>	<u> 75</u>	<u> 928</u>
1150	30	773
<u> "</u>	<u> 60</u>	<u> 795</u>
1350	20	613

Table VI

These results indicate that at 1150° the maximum activation is practically reached in 30 minutes. However, this maximum is rather low, indicating that the temperature is too high. Around 1000° seems to be the ideal temperature. The time element also seems to play a part.

The method for activating our carbon which we have found most successful consists in placing the covered fire clay crucibles containing the impure carbon in a cold muffle furnace, starting the fire and allowing it to burn at its maximum temperature two and one-half hours. (A temperature around 1000° C. is attained.) The fire is then stopped. The crucibles are allowed to remain in the furnace another half hour. They are then removed and cooled in air. The iodine number of activated carbon prepared in this manner will usually lie above 1000. The highest value yet obtained is 1157 which was on some carbon which had been reheated. The highest value obtained with a single heat treatment by the above method is 1120.

The final state of activation seems to depend to some degree upon the method of preparation and upon the

treatment before heating. Carbon made using a slight excess of chlorine is more easily activated than carbon made using the theoretical amount of chlorine. Carbon placed in the crucibles either dry or wetted with water is more easily activated than carbon which has been wetted with Skelly Solve. Wetting a carbon before heating has the advantage of greatly increasing the apparent density of the finished carbon. As an example, a dry packed carbon had an apparent density of 0.029 g./cc. after heating, a carbon wetted with water before heating had an apparent density of 0.10 g./cc. after heating, while a carbon which was wetted with Skelly Solve before heating had an apparent density of 0.13 g./cc. after heating. The final apparent density is dependent not only on the wetting agent used but also on the pressure used in packing the crucible. (Apparent densities are determined by filling a 50 ml. graduated cylinder with carbon, tapping until the volume is constant, reading the volume, and then weighing the carbon.

It is evident that the apparent density of a carbon can be substantially modified by proper treatment before heating. After a carbon has been heat treated, it does not lend itself well to such modification as can be shown by the following data. One of our activated carbons having an apparent density of 0.067 g./cc. was wetted with three different liquids, then dried, and new determinations of apparent densities made on the dried carbons.

	Apparent density
Wetted with benzene	0.070
Wetted with Skelly Solve	0.078
Wetted with water	0.088

A dense carbon has many economical advantages over a light carbon--more carbon can be heated in a given space, handling costs will be less, and less treated liquid will be retained by the carbon.

It was not considered advisable to evaluate our activated carbon solely on the results given in Table IV. In order that our carbon might be compared with other activated carbons in other laboratories, four samples of 50-100 g. and with an iodine number around 1050 were prepared and sent to the laboratories of the following companies: The Great Western Sugar Company, The American Sugar Refining Company, The Darco Corporation, and Industrial Chemical Sales. The last two companies are the two leading producers of activated carbon in the United States. The trade names for their carbons are Darco and Nuchar, respectively. Reports from the laboratories of the above companies will now be given.

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THE GREAT WESTERN SUGAR COMPANY:

COMPARISON OF A NEW ACTIVATED CARBON

FROM THE UNIVERSITY OF KANSAS WITH DARCO

A sample of a new decolorizing carbon from the Uni-

versity of Kansas was sent to this laboratory for test to determine whether it was superior to other good commercial carbons.

Evaporator thick juice from Ovid was treated with varying quantities of the two carbons in a series of parallel tests, and the color adsorption measured with the Lange colorimeter. Citric acid turbidity was also measured.

Nine 200 ml. portions (255 grams) of thick juice of 66.3% dry substance were measured into 500 ml. Erlenmeyer flasks. Sufficient water was added (70 ml.) to each to reduce the dry substance to 50%. The flasks were set in a water bath at 80° C. and after the juices had attained a temperature of 75° C. carbon was added in quantities ranging from 0.0 to 1.0% carbon on dry substance. After standing with frequent shaking for 30 minutes, a small amount of Filter-Cel was added and the flask contents poured onto a Buchner filter coated with Filter-Cel and filtered clear. Approximately 7 grams Filter-Cel was used inclusive of the filter coating.

The measurements as to color and citric acid turbidity are shown in the following table:

<u>Test No.</u>	<u>Kind of carbon</u>	<u>% Carbon on D. S.</u>	<u>Color Adsorption</u>	<u>Citric acid turbidity</u>
0	none	none	30	0.3
1	K.U.	0.1	27	0.2
2	Darco	0.1	26	0.3
3	K.U.	0.2	27	0.3
4	Darco	0.2	26	0.3
5	K.U.	0.5	25	0.3
6	Darco	0.5	24	0.3
7	K.U.	1.0	23	0.2
8	Darco	1.0	22	0.2

There is little difference between the two carbons. The small difference in color adsorption cannot with certainty be detected by visual comparison.

The new carbon is extremely light and "fluffy". Per unit volume it is approximately half as heavy as Darco. Unlike Darco, it "pours" readily.

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THE AMERICAN SUGAR REFINING COMPANY:

Letter from Mr. Louis A. Wills:

Report on your sample of activated carbon previously received has just come over from our laboratory and we are enclosing a copy herewith. You will note that your carbon in tests on two different sugar materials showed a decolorizing value higher than that of one of the commercial carbons, which in this case is one widely used in the United States and is the carbon that we ourselves use for certain special decolorizing work. The "No. 13 standard" mentioned in Mr. Bastone's report is one of the darkest grades of brown sugar (soft, refined sugar), and the test thereon constitutes a test on what we call low-grade or low-purity material. The washed sugar liquor is a solution of the raw sugar that we take into our refinery, after same has been washed in the centrifugal machines to free the crystals from adhering molasses or mother liquor. The test on this material shows the effect of your carbon on high-purity sugar material.

We shall be interested in learning of any further developments that you may make with this carbon.

Laboratory report by Mr. L. Bastone:

The new carbon was tested by comparing its action with that of a commercial carbon in two different grades of sugar liquor, as shown below.

The liquors at 50° Bx. were heated to 80° C. in a water bath. At this temperature the carbon was added to and incorporated with the liquor with constant stirring for a period of 20 minutes. A blank sample of liquor was also heated along with the treated samples. At the end of this treatment a small amount of earth was added to each liquor and each was filtered through paper. The color of each filtrate was determined in the Lovibond.

No. 1. Test

Liquor from No. 13 standard was treated with 0.5% carbon on solids:

	Test Liquor	U. of K. Carbon	Commercial Carbon
°Bx.	54.8	54.5	53.5
pH	5.2	5.2	5.2
Color 1/8" cell	366	175	199
Color per 100 solids	668	321	372
% Color removal	-	51.95	44.31

No. 2. Test

Press filtered washed sugar liquor was treated with

0.1% carbon on solids:

	Test Liquor	U. of K. Carbon	Commercial Carbon
°Bx.	57.0	58.7	57.7
pH	6.8	6.5	6.7
Color 1" cell	28	9	12
Color per 100 solids	52.8	18.1	24.8
% Color removal	-	65.72	53.03
	- - - - -		

DARCO CORPORATION:

We have received a report from our Research Laboratory regarding tests conducted with the sample of activated carbon that you sent us recently, which show the following data for the material.

The moisture of the sample as tested was 2.5%, other properties as listed below are expressed on the dry basis. The ash content was found to be 1.13%; the apparent density 0.186 gram per cc. equivalent to 11.6 lbs. per cubic foot tightly packed; the pH of a water extract 6.85; percentage of water solubles 0.34, and of total solubles 1.02; screen analysis 54.1% passing 100 mesh, 34.83% passing 200 mesh, 24.38% passing 325 mesh.

The relative efficiency as compared with the sample of DARCO that we sent you, the basis of comparison being the decolorization of a molasses solution, showed 80% R.E. for your carbon at 50% decolorization and 72.5% at 90%

decolorization.

The enclosed copy of our Laboratory Manual for Analyzing and Testing Decolorizing Carbons contains the procedures used in obtaining this data.

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INDUSTRIAL CHEMICAL SALES:

We acknowledge receipt of your letter of Sept. 14th and, at the same time, we have our Research Laboratory's report on the sample of carbon which you were good enough to submit. On the basis of our tests, we find it has a Molasses Value (on dry carbon) of 300 and an Iodine Value of 97, which indicates a product of high quality.

Of course, it is not possible for us to comment further in regard to its specific application to any product because of the peculiarly selective character of activated carbons in general, and the only way in which you can determine its real efficiency is to apply it in some commercial or semi commercial way.

Am I correct in assuming that the sample submitted has been prepared in the Laboratory? Cost is also an important factor.

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The reports from the two sugar companies are very favorable. It was hoped that the Darco and Nuchar people would give a more extensive report covering a larger number of tests.

We believe a word or two of explanation concerning the last two reports should be made. The carbon which Darco used in making comparisons with our carbon was one of their very special grades and sells for 15-1/2 cents per pound in ton lots (quotation of October 25, 1940). Industrial Chemical Sales, manufacturers of Nuchar, says the tests indicate a product of high quality. The iodine value of 97 means that 0.5 grams of our carbon removed 97% of the iodine from 100 ml. of solution containing 2.7 g. iodine per liter. "A good activated carbon will remove from 70 to 90 per cent of the iodine in such a test."²⁰ As to the molasses value, Mr. Wrench said the following in another correspondence: "The Molasses Values of NUCHAR vary from as low as 90 to as high as 500. However, it is our experience--and that of others--that you cannot judge entirely by the Molasses Value, because there are a number of other factors that enter into any particular decolorizing and deodorizing result. For example, we have instances where, on a particular product, a carbon with a 100 Molasses Value would do a better job than one having a Molasses Value of 500."

In order to get a more detailed comparison of our activated carbon with other activated carbons, two samples of our carbon designated as KUL and KU2 were prepared by slightly different methods and compared with six commercial carbons. These comparisons were made by preparing

adsorption isotherms for all eight carbons on three different solutions--iodine, phenol, and brown sugar solutions. While none of these tests can be used alone to predict definitely what can be expected of a carbon in a commercial process, it is hoped that these three tests will give some indication of what might be expected.

The iodine adsorption is used frequently as a control test. In general, it appears to be more indicative of the ability to remove odors and flavors rather than color bodies.²⁰ Phenol adsorption is an indication of the ability of a carbon to adsorb odors and flavors.²¹ The removal of color from brown sugar solutions should be an indication of what might be expected of our carbon if used in sugar refining.

The six commercial carbons used in making these comparisons will henceforth be designated by letters. Of the five carbons, other than Norite, three are manufactured by the Darco Corporation and two by Industrial Chemical Sales, a division of the West Virginia Pulp and Paper Company. The following brief explanation of these carbons is given along with cost per pound in ton lots F.O.B. shipping point. (Quotations are of October 1940.)

- A 15-1/2¢ A special carbon.
- B 10¢
- C 5-1/2¢ Used in water purification.
- D 6-1/2¢ Used in refining corn and beet sugars
- E 3-1/2¢ Used in water purification.
- F Norit

The only difference in the preparation of the KU carbons lies in the fact that KUL was packed in the crucible dry and KU2 was wetted with Skelly Solve before being packed into the crucible. Both carbons were heated under as near the same conditions as possible. As a result of wetting with Skelly Solve, KU2 has three to four times the apparent density of KUL.

Adsorption isotherms were drawn with the aid of Freundlich's equation which may be stated as follows:

$$\frac{x}{m} = kc^{\frac{1}{n}}$$

In this expression

x refers to the total amount of impurity adsorbed from a fixed quantity of solution.

m is the amount of activated carbon used.

c is the residual concentration of impurity in solution, after the adsorption has been completed.

If a given quantity of solution of a given concentration is treated with different amounts of carbon we can get values of $\frac{x}{m}$. If these values of $\frac{x}{m}$ are plotted against values of c on logarithmic paper, a straight line will result if the adsorption is following Freundlich's equation. Theoretically it should not be necessary to determine more than two points. Actually, it is best to determine at least four.

The iodine adsorption isotherms were determined

as follows: Decreasing amounts of dry carbon were added to 100 ml. of 0.04 N iodine in water solution (containing 508 mg. of iodine per 100 ml. solution), agitated occasionally for 20 minutes and filtered. Fifty ml. of the filtrate were titrated with standard sodium thiosulfate solution, using starch as an indicator. Knowing the iodine equivalent of the thiosulfate solution one can calculate c from the results of titration. The value of x is equal to $508 - c$.

The phenol adsorption isotherms were determined as follows: Decreasing amounts of dry carbon were added to 100 ml. of 0.025 N phenol in water (containing 235 mg. of phenol per 100 ml. of solution), agitated occasionally for 20 minutes and filtered. Twenty-five ml. of the filtrate was transferred to a 250 ml. glass stoppered bottle and diluted to around 100 ml. An excess of 0.1 N KBrO_3 solution containing an excess of NaBr was added along with 10 ml. of 4 N H_2SO_4 . The solution was shaken, and fifteen minutes was allowed for the reaction to come to equilibrium. An excess of KI solution was then added, and the liberated iodine was titrated with standard sodium thiosulfate solution. From the difference between the amount of bromine liberated by the KBrO_3 and the bromine found to be present by titration with thiosulfate, one can calculate the amount of bromine which has reacted with the phenol to form tribromophenol, and from this calculate c . The value of x is equal to $235 - c$.

The color adsorption isotherms which were run on

brown sugar solutions were determined as follows: Decreasing amounts of activated carbon were added to 100 ml. of a brown sugar solution containing 150 g. brown sugar per liter of solution. The sugar solution was placed in a water bath at 70° C., shaken several times over a period of 20 minutes, filtered until sparkling clear, and the color remaining was determined by measuring the percentage transmittance of light through the sugar solutions compared to distilled water as a standard. The percentage transmittance was determined with a Cenco-Sheard spectrophotometer. Light having a wave length of 4500 Angstroms was used in this work because it had a greater adsorption in brown sugar solutions than light of another wave length.

In order to calculate the values of x and c in Freundlich's equation from the percentage transmittance we make use of the following relationship.

$$I/I_0 = e^{-kdc}$$

Where I = the intensity of the light emerging from the solution

I₀ = the intensity of light entering the solution.

e = the base of natural logarithms.

k = a constant.

d = the distance which the light travels through the solution.

c = the concentration of the colored substance in the solution.

The above expression can be written

$$\ln I/I_0 = -kdc$$

or $\ln I_0/I = kdc$

Since the distance d was constant in this work, we can substitute a new constant K for kd. Solving the above equation for c and changing to logarithms to the base 10, we have

$$c = \frac{2,303 \log I_0/I}{K}$$

In order to evaluate the constant, the above equation was solved for K and measurements of I_0/I were made on three solutions containing respectively 50, 100, and 150 g.

brown sugar per liter of solution. The value of K determined by this method was found to be 0.0054. Assuming that the original brown sugar solution contained 150 color units, the color units remaining after carbon treatment would be given by the expression

$$c = 426 \log \frac{I_0}{I}$$

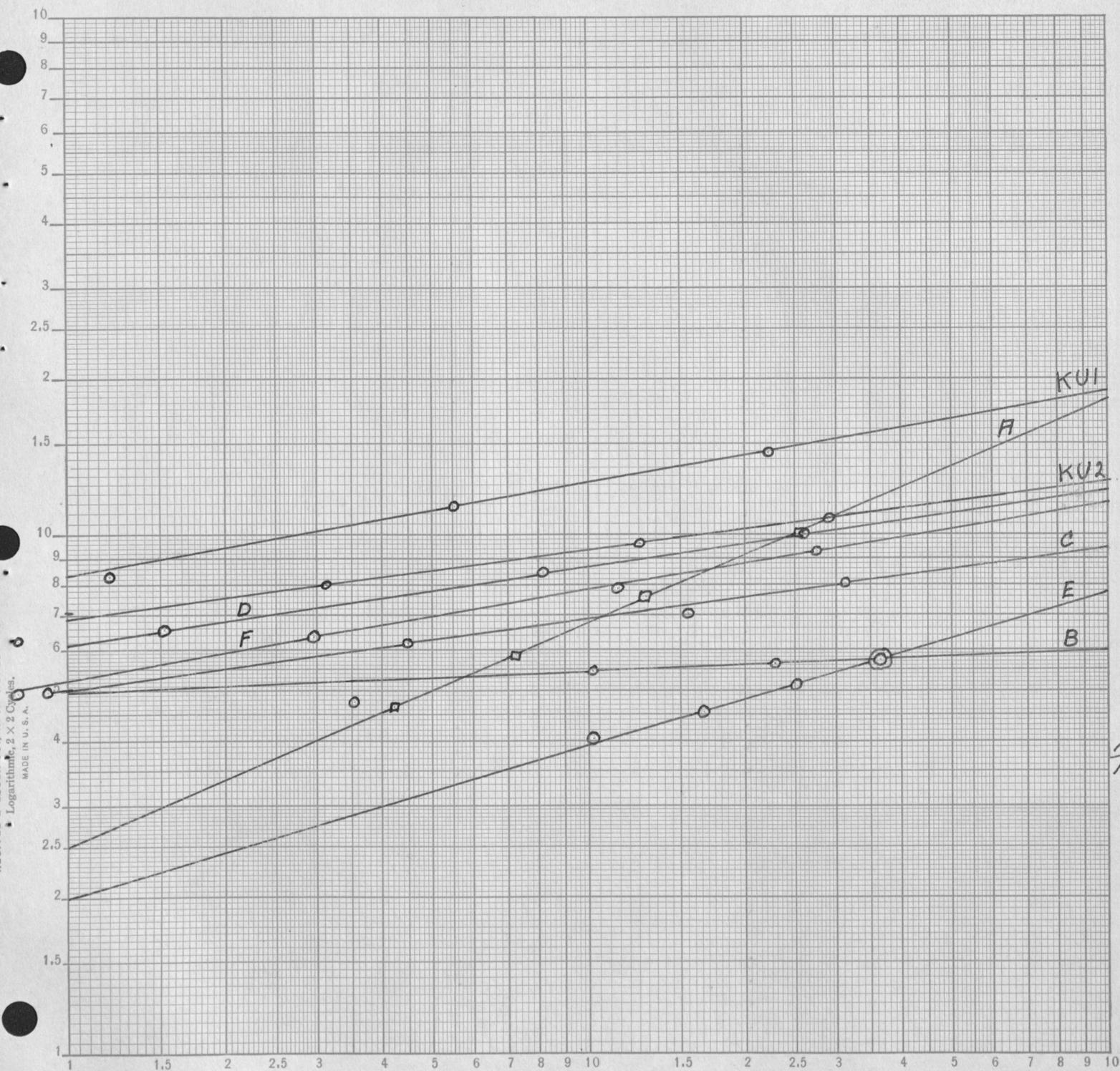
The value of x in Freundlich's equation is then equal to 150 - c.

The data collected according to the procedures just described will now be given. It contains the results obtained using three different solutions and eight different activated carbons on each solution. The adsorption isotherms accompany the data.

Table VII. Adsorption of iodine from 100 ml. of 0.04 N iodine solution by decreasing amounts of activated carbon. The quantities c , x , and m are given in milligrams.

<u>Carbon</u>	<u>c</u>	<u>x</u>	<u>m</u>	<u>$\frac{x}{m}$</u>
KU1	3.9	504	800	.630
	12.0	496	600	.826
	55.6	452	400	1.13
	222	286	200	1.43
KU2	8.1	500	800	.625
	32.3	476	600	.793
	125	383	400	.957
	293	215	200	1.074
A	42.3	466	1000	.466
	72.5	435	750	.581
	129	379	500	.757
	256	252	250	1.007
B	35.5	473	1000	.473
	102	406	750	.541
	228	280	500	.560
	365	143	250	.572
C	9.2	499	1000	.499
	44.8	463	750	.618
	156	352	500	.703
	307	201	250	.803
D	4.4	504	1000	.503
	15.1	493	750	.657
	81.2	427	500	.852
	258	250	250	1.000
E	101	407	1000	.407
	166	342	750	.456
	251	257	500	.514
	364	144	250	.576
F	8.0	500	1000	.500
	29.3	479	750	.639
	114	394	500	.788
	276	232	250	.928

Iodine Adsorption Isotherms



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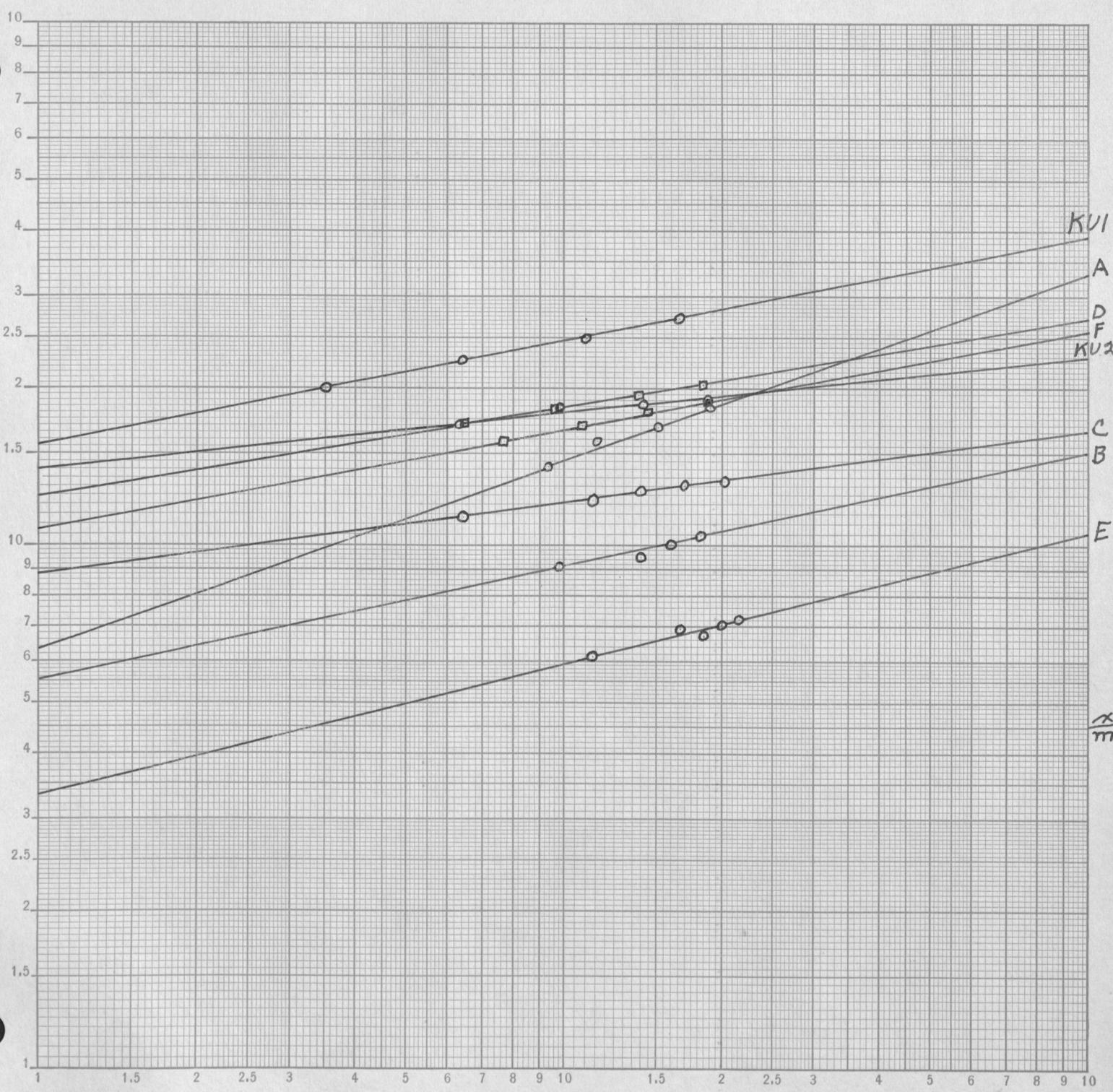
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Table VIII. Adsorption of phenol from 100 ml. of 0.025 N phenol solution by decreasing amounts of activated carbon.

The quantities c , x , and m are given in milligrams.

<u>Carbon</u>	<u>c</u>	<u>x</u>	<u>m</u>	$\frac{x}{m}$
KU1	35.0	200	1000	.200
	64.6	170	750	.227
	111	124	500	.248
	167	68	250	.272
KU2	63.5	171	1000	.171
	98.3	137	750	.183
	142	93	500	.186
	187	48	250	.192
A	93.2	142	1000	.142
	116	119	750	.159
	151	84	500	.168
	189	46	250	.184
B	98.0	137	1500	.0913
	140	95	1000	.095
	160	75	750	.100
	183	52	500	.104
C	64.7	170	1500	.113
	113	122	1000	.122
	140	95	750	.127
	170	65	500	.130
	202	33	250	.132
D	64.6	170	1000	.170
	96.7	138	750	.184
	138	97	500	.194
	184	51	250	.204
E	113	122	2000	.0610
	166	69	1000	.0690
	185	50	750	.0667
	200	35	500	.0700
	217	18	250	.0720
F	76.7	158	1000	.158
	108	127	750	.169
	145	90	500	.180
	188	47	250	.188

Phenol Adsorption Isotherms



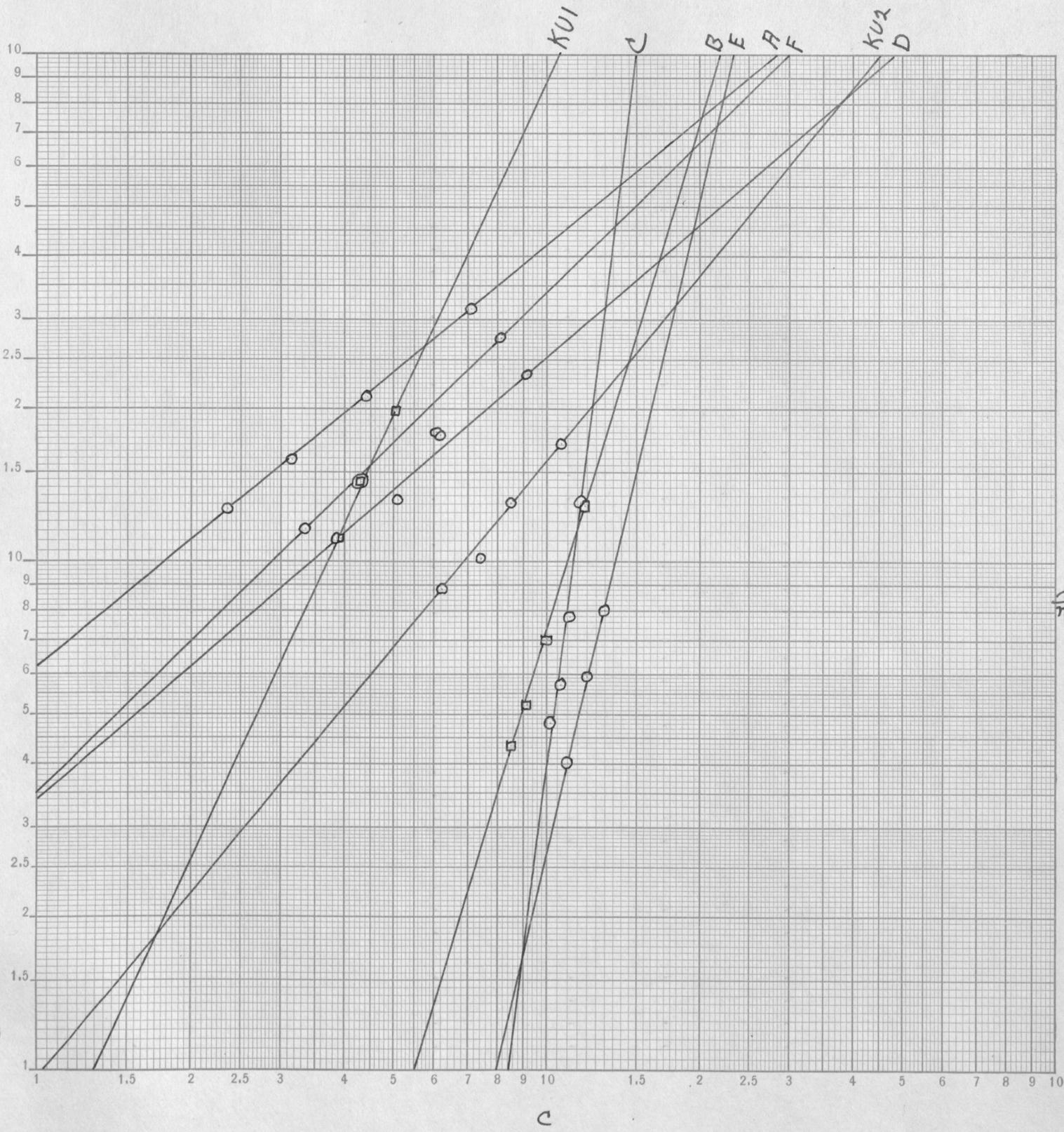
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C

Table IX. Adsorption of color from a brown sugar solution, containing 150 g. brown sugar per liter of solution, by decreasing amounts of activated carbon. The quantities c and x are given in color units, m is given in milligrams.

<u>Carbon</u>	<u>Percentage Transmission</u>	<u>c</u>	<u>x</u>	<u>m</u>	<u>$\frac{x}{m}$</u>
KU1	80.9	39.3	111	1000	.111
	79.3	43.0	107	750	.143
	76.0	50.8	99.2	500	.198
KU2	71.5	62.2	87.8	1000	.0878
	67.0	74.2	75.8	750	.101
	63.2	85.2	64.8	500	.130
	56.0	107	42.7	250	.171
A	88.2	23.4	127	1000	.127
	84.3	31.5	119	750	.158
	78.8	44.3	106	500	.211
	68.1	71.2	78.8	250	.315
B	63.1	85.1	64.9	1500	.0433
	61.0	91.5	58.5	1100	.0522
	58.0	101	49.3	700	.0705
	52.8	118	32.0	250	.128
C	57.7	102	48.0	1000	.048
	56.0	107	43.0	750	.057
	54.8	111	39.0	500	.0776
	53.0	117	33.0	250	.130
D	81.2	38.6	111	1000	.111
	76.0	51	99	750	.132
	71.7	61.6	88.4	500	.177
	61.0	91.5	58.5	250	.234
E	55.2	110	40	1000	.040
	52.2	120	29.7	500	.0593
	49.6	130	20	250	.080
F	83.4	33.5	116.5	1000	.116
	79.5	42.4	108	750	.144
	72.0	60.7	89.3	500	.179
	64.5	81.1	68.9	250	.276

Color Adsorption Isotherms



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m

The use of adsorption isotherms permits one to compare activated carbons with a minimum number of tests. As a general rule, it can be said that the larger the value of x/m and the smaller the slope of the isotherm, the more efficient is the carbon.

The relative amounts of two carbons which are required to remove an impurity to a given concentration can easily be calculated. At the desired final concentration c , we read the values of x/m for each of the carbons. Suppose these carbons are A and E on the iodine adsorption isotherms, then--

$$\frac{m_A}{m_E} = \frac{x/m_E}{x/m_A}$$

If we want the final concentration to be 100 mg. iodine per 100 ml. solution then--

$$\frac{m_A}{m_E} = \frac{392}{675}$$

In other words, to get a solution of a final concentration of 100 mg. iodine per 100 ml. solution, it would require only 58% as much carbon A as carbon E, or carbon A is 1.72 times as efficient as carbon E for the specified final concentration.

The same results can be arrived at with a pair of dividers. The distance between A and E where c is 100 is taken. This distance is then transferred to the right edge of the graph. One point of the divider is placed on the "1" line between the two cycles. Measuring the distance downward, the other point of the divider will rest on .58, measuring upward, the point will rest on 1.72.

It often happens that the isotherms of two carbons cross. Where this happens, their efficiencies are the same at that point but change on either side. Considering the two curves, A and C, on the iodine adsorption graph, if the final concentration desired lies to the left of the point of intersection, C is more efficient than A. On the other hand, if the final concentration lies to the right of the point of intersection, A is more efficient than C. If, therefore, we are choosing between A and C and all their other properties are equal, and the prices are the same, we would choose C if the solution is to be highly purified in one treatment and A if counter current decolorization is to be used.

The gas adsorption capacity of our carbon was compared with the gas adsorption capacity of cocoanut charcoal, using air, propane, and chlorine. The cocoanut charcoal used in these tests came from the U. S. War Department and was supposed to have high adsorptive capacities.

A carbon used for adsorbing gases should have a high apparent density, so it will not be too bulky, and it should be granular in order to allow circulation of the gases.

It was found that our carbon could be produced in a granular form about one-third as dense as cocoanut char-

coal and rigid enough to be handled without crumbling. The method consisted in barely wetting with Skelly Solve, and compressing under pressure, followed by heating until sufficiently activated.

The gas adsorption measurements were carried out in a specially built adsorption tube as shown in Figure IV. A typical run may be described as follows: The adsorption tube was weighed empty. The ground joint was removed and a quantity of carbon was added to the tube through a funnel. The joint was replaced and the lower part of the tube and contents were heated to 400° C. for thirty to forty minutes and under a pressure of 1 mm. mercury. The stop cocks were then closed and the adsorption tube was cooled and weighed. The gas to be adsorbed was then passed through the tube. During adsorption, the tube was kept in a water bath at 25° C. The part of the adsorption tube above the ground joint was filled with glass wool to catch any carbon dust which might be blown up. The gas was allowed to flow one hour after it could be easily detected at the exit. The stop cocks were then closed and the tube and contents again weighed. Since one weighing had to be made with the tube evacuated, the other two weighings were corrected to what they would have been if the tube had been evacuated in these cases also. The density of carbon was taken as 2.5.

Adsorption measurements could be made on all three

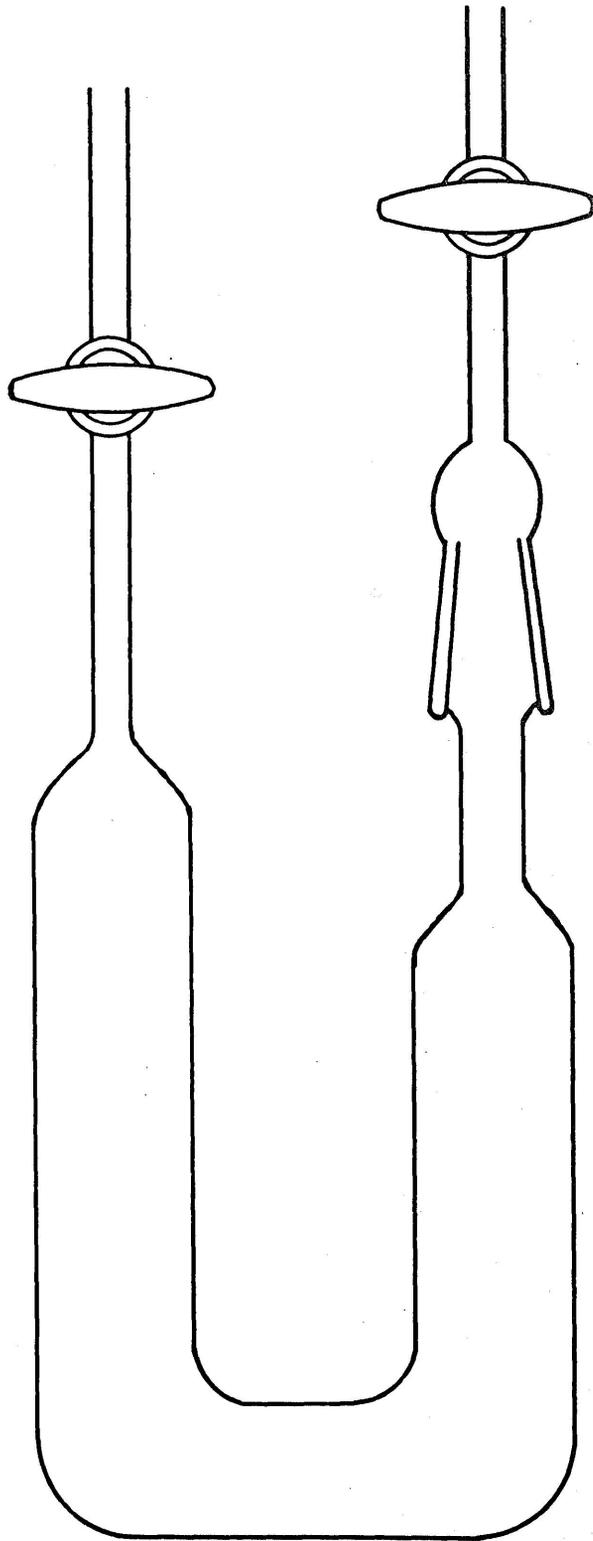


Fig IV

gases using the same carbon if the measurement on chlorine was made last and if the tube and contents were heated and evacuated between the passage of each gas. The chlorine could not all be removed from either our carbon or cocoanut charcoal by heating to 400° C. for thirty to forty minutes under 1 mm. mercury pressure. Cocoanut charcoal retained 29% of its adsorbed chlorine while our granular carbon retained 19%.

Results obtained on gas adsorption are given in the following table:

<u>Kind of Carbon</u>	<u>Weight of Carbon</u>	<u>g. air per g. carbon</u>	<u>g. propane per g. carbon</u>	<u>g. chlorine per g. carbon</u>
cocoanut charcoal (20 mesh)	32.34 g.			0.383
cocoanut charcoal (40 mesh)	27.11 g.	0.0273	0.109	0.403
KU2	8.88		0.155	0.471
KU (granular)	12.71	0.0126	0.184	0.588

Table VII

CONCLUSION

New methods for the production of activated carbons have been described. The final state of activation depends upon the duration of the heat treatment and upon the temperature. The adsorption data given indicates

that these new carbons are very highly activated and that they will compare favorably with the best commercial carbons now produced. The KU carbons seem to be best suited for the adsorption of gases and for the removal of odors and flavors.

Part III

Chlorination of n-Butane and Pyrolysis
of Chlorinated n-Butane

INTRODUCTION

Ninety years ago, Frankland²² observed that a dry mixture of chlorine with butane reacted immediately on exposure to diffused daylight.

Schoyen²³ found that chlorine and butane did not react in the dark, but when butane over water in a flask of white glass was quickly mixed with an equal volume of chlorine, and the flask placed in bright daylight, reaction took place immediately with the formation of HCl and a liquid insoluble in water.

Ronalds²⁴ found that butyl chloride was formed when butane from American petroleum reacted with two volumes of chlorine in the presence of light.

Much of the work done on the chlorination of butane in recent years has had as its object the production of the monochloro derivatives.

Hass and Weston²⁵ in 1932 studied the production of butenes from 1- and 2-chloro butane. They obtained their monochloro butane, using a ratio of butane to chlorine of 10:1. They obtained a product containing 90.3% mono- and 9.7% polychloro derivatives. Of the monochloro derivatives, 63% was 2-chloro and 37% 1-chloro butane. This is about the ratio one would expect according to the rules of chlorination given by Hass²⁶ in 1936.

Kharasch and Brown²⁷ in 1939 made the following generalizations concerning chlorination of aliphatic

hydrocarbons. "Substitution takes place on a secondary carbon atom in preference to a primary. A second chlorine atom tends to substitute as far from the first as possible. It is difficult to get two chlorine atoms on one carbon." The above generalizations can also be obtained from the rules of Hass.

Workers in the past who have produced dichloro butanes have frequently started with the monochloro butanes which were in turn made from the corresponding alcohols.

Tishchenko²⁸ states that the chlorination of 2-chloro butane in liquid phase yields all four isomeric dichlorides. Chlorination of 1-chloro butane in liquid phase at 35° to 40° C. with illumination gave the following yields of the four possible isomeric dichlorides:

1, 1	3%	1, 3	50%
1, 2	17%	1, 4	25%

Muskat and Northrup²⁹ chlorinated 1-chloro butane in the vapor phase with illumination. They separated the isomers and determined the yield of butadiene obtained from each isomer by passing over hot soda lime in an iron tube. The best yield reported was 29.6% from the 1, 3-dichloride.

The literature contains more references on obtaining butadiene from dihydroxy compounds than from dichloro compounds.

It seems that very little work has been done toward the production of trichloro butanes by direct chlorination.

Practically no physical constants are available on the nine possible isomers of trichloro butane. Charon³⁰ gives the boiling point of 1, 2, 3-trichloro butane as 79° to 80° at 32 mm.

No reference to the pyrolysis of trichloro butanes has been found.

CHLORINATION OF n-BUTANE

The n-butane used in this work was a commercial grade (97% n-butane) obtained from The Matheson Company.

Chlorination can be effected by mixing the chlorine and butane in a 'T' tube in the dark and then passing this mixture into a larger reaction tube where it is reacted in the presence of light or another catalyst.

It has been found that if iron wire is used as a catalyst at temperatures above 150° C., chlorination is accompanied with considerable decomposition--using equal volume ratios of chlorine and butane.

Water has been used as a catalyst in vapor phase chlorination. Water vapor was introduced by bubbling the butane through water at room temperature. The presence of water vapor increased considerably the ratio of 1-chloro butane to 2-chloro butane when the ratio of chlorine to butane was 2:1.

It must be remembered that in this work we were interested mainly in obtaining the di- and trichloro

derivatives. We have found that in the vapor phase chlorination of n-butane, the smoothest reaction and the cleanest product could be obtained by using the dry gases and reacting them in the presence of diffused daylight or artificial light.

The vapor phase chlorinator used in this laboratory is shown in figure V. The reaction tube is pyrex with an inside diameter of 22 mm. All the gases used were measured through flow meters. All the butane and half the chlorine used was mixed in the 'T' tube at A. The 'T' tube and the first 8 to 9 cm. of the reaction tube were kept dark by wrapping. The first reaction took place in the lighted section B. C is a condenser built into the reaction tube, and D is a vessel for collecting the condensed vapors. D is provided with a stopcock to facilitate emptying. At E the other half of the chlorine is added through two side arms. The reaction tube around E and for 10 to 15 cm. below E must be kept wrapped to prevent burning. The final reaction takes place in the lighted section B'. The vapors condense and are collected in the container F and in the HCl absorber.

The product desired will determine the ratio of chlorine to butane which one should use. Ordinarily we used slightly more than two volumes of chlorine to one of butane. The product obtained contained from 10% to 20% monochloro butanes, 50% to 60% dichloro butanes, 30% to

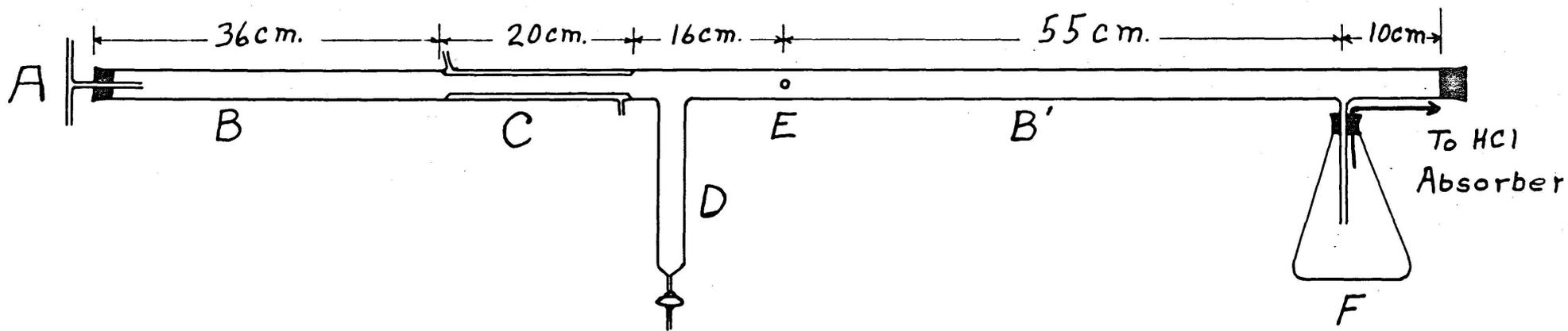


Fig V

40% trichloro butanes, and very little tetrachloro butane. Increasing the ratio of chlorine to butane increased the tendency for the gases to burn.

The type of chlorinator described will use one mol of butane per hour. If the butane and chlorine are passed through at a faster rate, the reaction zones will become excessively hot and decomposition will result. When sufficient light is present, 100% of the chlorine and 90% to 95% of the butane will be utilized (ratio of chlorine to butane being 2:1).

This chlorinator was designed to use a large percentage of butane without recycling and to give good yields of di- and trichloro butanes without the tetrachloro butane being formed. If two volumes of chlorine and one volume of butane were mixed and allowed to react, the chances for the formation of tetra chlorides would be increased and less butane would be utilized. In the apparatus as described, the same ratio of chlorine to butane can be used but the ratio at any place in the apparatus is never greater than 1:1.

The oil obtained from the vapor phase chlorination can be separated by distillation into--

	Boiling points
2-chloro butane	68
1-chloro butane	78.5
2, 2-dichloro butane	100-103
1, 1 and 2, 3-dichloro butane	113-116

1, 2-dichloro butane	121-125
1, 3-dichloro butane	131-136

Table VIII

Some of the above boiling points are given over a rather wide range. It seems that no accurate data has been collected on these boiling points. The dichloro derivatives 1, 1 and 2, 3 cannot be separated with ordinary rectifying columns. The 1, 4 derivative, boiling point 161-3, cannot be separated from the lower boiling tri-chloro derivatives as they boil at the same temperature.

The dichloro derivatives produced by the direct chlorination of butane in the vapor phase are distributed approximately as follows. The separation was made by slow distillation in a Vigreux column 70 cm. long made of 22 mm. pyrex tubing.

Derivative	% by weight	Collected between
2, 2	7	95-108
1, 1	5	108-118
2, 3	30	108-118
1, 2	25	118-128
1, 3	25	128-140
1, 4	8	

Table IX

Since 1, 1 and 2, 3 were not separated from each other the values given for them were arrived at by taking

the following facts into consideration. The percent of 1, 1 formed will be low for two reasons. In the first place, 1, 1 must be formed from the 1-chloro butane which in turn makes up less than one-third of the two monochloro derivatives. In the second place, it is known that the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution. (Rule 9)²⁶

The value given for the 1, 4 derivative cannot be determined directly. An approximate value could be arrived at by taking into account the facts mentioned above concerning the 1, 1 derivative. An indirect procedure for determining the amount of 1, 4 derivative was carried out as follows. The chlorinated butanes boiling above 140° C. at atmospheric pressure were distilled under reduced pressure until all the 1, 4 derivative had distilled over. The distillate was then analyzed for chlorine. From the analysis, the ratio of di- to trichloro derivatives in the distillate could be determined. Then from the amount of distillate, the amount of 1, 4 derivative could be determined.

The chlorination of the two monochloro butanes has been studied under several conditions. The purpose of this study was to determine the percentages of the various dichloro derivatives produced, and to determine what effect chlorination conditions have upon the yield of the

various derivatives.

The monochloro butanes used in this work were obtained by the chlorination of butane as previously described. They were separated from each other and from the other chlorides by two slow fractionations by a column 120 cm. long made of 25 mm. pyrex tubing and packed with glass beads. The 2-chloro butane was collected from 64° to 69° C. at 740 mm., and the 1-chloro butane was collected from 74° to 79° C. at 740 mm.

Each of these derivatives was chlorinated in the vapor phase by a method similar to that described by Muskat and Northrup²⁹. The 2-chloro butane was chlorinated in the liquid phase under two different conditions. In one case the 2-chloro butane was diluted with an equal volume of glacial acetic acid, and in the other case the 2-chloro butane was diluted with an equal volume of CCl₄ before chlorination. Chlorination was effected in Kjeldahl flasks in the presence of light. The chlorine was conducted to the bottom of the liquid through a capillary tube at the rate of one-half mol per hour. The liquid was cooled from time to time if necessary to prevent unreacted material from being carried away with the HCl.

When the reaction was stopped, the CCl₄ was removed from the other products by distillation. The acetic acid was removed by extraction with water. The following results were obtained on distillation.

Vapor phase chlorination		Liquid phase chlorination	
I	II	III	IV
1-ClBu	2-ClBu	Acetic Acid 2-ClBu	CCl ₄ 2-ClBu
31	28	25	30 % unreacted
49	51	39	43 % went to di
20	21	36	27 % went to tri

The dichloro derivatives produced were distributed as follows:

Derivative	I	II	III	IV
1, 1	13			
1, 4	12			
1, 3	37	28	24	25
1, 2	38	19	28	19
2, 2		21	12	23
2, 3		32	36	33

Table X

In the case of vapor phase chlorination, the yield of trichloro derivatives could be reduced by increasing the ratio of vapor to chlorine. In the case of liquid phase chlorinations, the yield of trichloro derivatives could be reduced by stopping the chlorination at an earlier stage; that is, when there is a larger percentage of unreacted monochloro butane present.

The percent of each of the dichloro derivatives produced as given in Table X was determined by one careful fractionation with a Vireux column 70 cm. long made

of 22 mm. pyrex tubing. The boiling ranges were the same as those given in Table IX.

The data in Table X indicates that chlorinating conditions probably play a part in determining the composition of the final product. Considering the chlorination of 2-chloro butane, the percent of each derivative produced by vapor phase chlorination and by liquid phase chlorination in CCl_4 is practically the same. Liquid phase chlorination in the presence of acetic acid shows quite different results. The data on chlorination in acetic acid has been verified by another run.

In the preparation of trichloro butanes, the oil obtained from the vapor phase chlorination of butane (using two volumes of chlorine to one of butane) is separated into mono- and dichloro derivatives and tri or higher chlorinated derivatives. The fraction containing the mono- and diderivatives is then chlorinated in the vapor or liquid phase without dilution, or in the liquid phase and using CCl_4 as a diluent. Liquid phase chlorination has proved to be the most satisfactory in this laboratory. It is essential that the chlorination be stopped, and the tri derivatives separated from the di, before the mol fraction of dichloro derivatives gets much below 0.5. In one trial run, two volumes of mono- and dichloro butane were diluted with one volume of CCl_4 and chlorinated in the liquid phase. Chlorine was introduced into the bottom of

the liquid through a capillary tube at the rate of one mol every two and one-half hours. Chlorination was stopped when about half the theoretical amount of chlorine had been added. Distillation gave 400 g. between 100° to 140°, and 600 g. above 140°. The fraction above 140° contains the small amount of 1, 4 dichloro derivative, the trichloro derivatives and higher chlorinated derivatives. In this particular case, the oil above 140° was analyzed for chlorine. The percent chlorine found was 66.0% to 66.5%. This analysis indicates that a good yield of trichloro butane had been obtained since the theoretical amount of chlorine should be 66.0%.

In this work, no attempt was made to separate the various isomers of trichloro butane. An attempt was made to separate the tri derivatives from the di and tetra derivatives. All the di derivatives, except 1, 4 could be removed by distillation to 140° C. at atmospheric pressure. The product remaining was nearly always distilled under reduced pressure to avoid decomposition.

Since no data on the boiling points of trichloro butanes was available, the composition of the distillate was determined from its refractive index. The following relationships were first determined.

Refractive index at 25° C.	% Chlorine
1.4610	62.5
1.4701	64.7
1.4748	66.1
1.4809	68.1
	BuCl ₂
	55.8
	BuCl ₃
	66.0
	BuCl ₄
	72.5

Table XI

The oil used as trichloro butane in this laboratory boiled above 140° C. at atmospheric pressure and had a refractive index less than 1.4800 at 25° C. The boiling range of this oil at 2 cm. of mercury pressure was 55° to 80° C.

Pyrolysis of Di and Tri Chloro Butanes

The purpose of this work was to produce unsaturated compounds which could be polymerized into useful substances.

Attempts to split out HCl from trichloro butanes by refluxing with 25% aqueous NaOH had little success. In one trial, a sample of oil boiling between 70° to 81° at 4 cm. was refluxed 16 hours with a 25% aqueous NaOH solution. A very small amount of gas was formed. Al-

though there was a large excess of NaOH present, most of the oil remained apparently unchanged. The oil was separated by steam distillation and dried. It had a refractive index of 1.4580 compared to 1.4620 for the original. This slight change could be accounted for by the presence of a few OH groups. In another trial, 0.5 mol of trichloro butane was boiled for three hours with solid NaOH. No gas was given off. Upon distillation of the oil, about 10 ml. came over from 110° to 140° indicating that some HCl had been split off and probably formed $C_4H_6Cl_2$. Analysis for chlorine showed 58.0% chlorine.

If trichloro butane is added to an excess of 20% alcoholic KOH in the cold and the mixture warmed, a reaction takes place quite rapidly and much gas is evolved. In one trial, water was added to the mixture after the reaction had subsided and the remaining oil was separated and dried. It had a refractive index of 1.4450 compared to 1.4750 for the original. The water had the characteristic unsaturated odor common to unsaturated hydrocarbons.

Although the reaction between solid NaOH and trichloro butane is slow even at 140° C., the reaction between solid KOH and trichloro butane proceeds quite rapidly. The reaction starts at room temperature and evolves heat. A brown amorphous mass rises to the surface and soon all the material present takes on the same appearance. Upon the addition of water, an oil separates which has an index

of refraction of 1.4600 compared to 1.4750 for the original. This oil on analysis was found to contain 56.0% to 56.2% chlorine.

The above methods for splitting off HCl and producing unsaturated derivatives didn't produce the desired results so high temperature reactions were studied. It was known that iron was an HCl splitting catalyst so it was tried in the following manner. A 30 cm. roll of iron gauze was placed tightly inside a 25 mm. pyrex tube and was heated in an electric furnace. The trichloro butane was passed through at the rate of 20 ml. per hour. Decomposition started at around 300° and at 500° considerable carbon was formed. The vapors were condensed in an ice bath. Upon distillation of the condensed oil, 25% came over below 140°, mainly from 65° to 100°. The oil above 140° represented unchanged material.

Passing chlorinated butanes over coarse soda lime in an iron tube at 500° C., gave unsaturated derivatives. However, much carbon was formed and the tube soon became clogged. Because of carbonization, the soda lime didn't take up all the HCl as it was formed. The soda lime seemed to act merely as a heat transfer medium, giving a large surface for contact. It does not seem to be necessary to remove the HCl as soon as it is split off. The tendency for the HCl to add back on at the double bond is small under the conditions of the experiment.

An iron tube filled with clay chips worked about the same as soda lime. The carbon formed soon closed the tube.

The most satisfactory apparatus for carrying out pyrolysis reactions consisted of a 25 mm. pyrex tube, four feet long and filled with 9 mm. glass tubing cut into two to three inch lengths. The heat for the reaction was supplied by an ordinary combustion furnace. The tube was long enough to extend several inches beyond each end of the furnace. One end of the tube was kept closed with a rubber stopper which could be removed and the tube could then be cleaned if necessary. The oil entered through a side arm sealed at right angles to the large tube. The oil was placed into a separatory funnel and its flow was regulated by adjusting the stopcock. If more head was needed to force the oil through the system, a small pressure could be applied to the liquid in the separatory funnel. The other end of the large tube was sealed to a 500 ml., long neck, distilling flask. The purpose of this distilling flask was to collect the unreacted oil which would condense at the end of the reaction zone. If it was desirable to recycle this oil, it could be drained from the flask and recycled. The side arm of the distilling flask led to the other receiving vessels which varied with the experiments. If it was desirable to determine the amount of butadiene formed, the gases after leaving the distilling flask were first bubbled through water maintained near 0° C. The HCl

would be absorbed and the low boiling monochlorides would be condensed and collect on the surface of the water. The butadiene and other light gases would pass on and be bubbled through a solution of bromine in carbon tetrachloride. The butadiene formed could be calculated from the butadiene tetrabromide remaining after distilling off the carbon tetrachloride and other lighter materials.

A number of determinations were made on the yields of butadiene obtained from the different isomeric dichloro butanes. The furnace temperature was around 500° C. and the dichloro butanes were passed through at the rate of 150 g. per hour. After the passage of a given quantity of dichloro butane, the oil which had collected in the distilling flask at the end of the reaction tube and the unsaturated monochlorides collected above the wash water were recycled. The oil which remained after the second passage through the hot tube was distilled and separated into the unsaturated monochlorides and the unreacted dichlorides. The CCl_4 solution of tetrabromobutadiene was distilled and all material boiling above 100° C. at 2 cm. pressure was taken to be tetrabromobutadiene. This material solidified upon cooling. Purification by recrystallization from CCl_4 gave crystals with a melting point of 117° C. The reason why the material doesn't solidify during the final stages of distillation is that there is present a stereoisomer whose melting point is much lower than 117.

The following table gives the results obtained from several different fractions of dichloro butane:

Column I Isomer of dichloro butane used.
 Column II Percent yield of butadiene based on the amount of $C_4H_8Cl_2$ which reacted.
 Column III Percent yield of C_4H_7Cl based on the amount of $C_4H_8Cl_2$ which reacted
 Column IV Percent yield of butadiene based on the amount of $C_4H_8Cl_2$ which reacted other than that which went to produce C_4H_7Cl .

<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
1, 2 and 1, 3 126 - 130	40	23	53
2, 2 99 - 105	7	35	15
1, 3 130 - 134	42	27	57
2, 3 and 1, 1 110 - 116	15	64	43
2, 3 and 1.1 107 - 119	16	66	47

Table XII

From the way in which the above data is tabulated, it is evident that as the percentage given in column III increase, the percentages in column II will decrease. The figures in columns II and III should add up to 100 if the only products formed were butadiene and C_4H_7Cl . The differ-

ence between their sum and 100 represents loss due to carbon formation, formation of lighter gases, evaporation losses, and retention of products by containers. This latter loss will become increasingly large as the amount of material worked with decreases. Ordinarily from 150 to 250 g. of material were used for each run.

In this work the butadiene was the product wanted. The C_4H_7Cl formed is an intermediate product and represents the first step in the formation of butadiene. No determinations were run to determine the yields one might expect of C_4H_7Cl if it were the product desired. Experience has shown that during the first passage through the furnace, a comparatively large amount of C_4H_7Cl is formed and then during the second passage much of this monochloride undergoes further reaction to form butadiene. If C_4H_7Cl was the product desired, it could probably be obtained with high yields by using a slightly lower furnace temperature or decreasing the time of contact with the hot surfaces. The oil collected at the end of the reaction tube should be separated into the mono- and dichloro derivatives before recycling.

Table XII indicates that the highest yields of butadiene are obtainable from the 1, 3-dichloro derivative. One might expect equally high yields from the 2, 3 derivative. It must be remembered that in the 2, 3 derivative there is present some 1, 1 derivative, probably 15% to 20%.

The low yield of butadiene from 2, 2-dichloro butane is expected since the removal of the second HCl would probably involve the removal of a chlorine atom from a double bonded carbon atom, which configuration is generally considered quite stable. If two HCl are removed, there would still be needed a shift in the double bond for the formation of butadiene. Such a shift, however, is considered to take place quite easily.

During the pyrolysis of 2, 2-dichloro butane, some observations were made which are not given in table XII. During the first passage of the dichloride through the hot tube, very little butadiene or any gas escaped past the wash water. There was lots of HCl formed and a good yield of C_4H_7Cl was present above the wash water. It seemed that 2, 2-dichloro butane lost one mol of HCl more easily than other dichloro butanes. During the second passage, much of the C_4H_7Cl was broken down as can be seen from the low yields of products obtained. Much more gas than usual passed through the bromine reactor without addition. This fact indicates the presence of low boiling pyrolysis products with probably one or two carbon atoms. It seems that if a compound of the formula C_4H_7Cl , having a chlorine atom attached to a double bonded carbon atom, is passed through a hot tube, there will occur the splitting of a C-C bond rather than the removal of HCl.

The pyrolysis of trichloro butanes was carried

out in much the same manner as has just been described for the dichloro butanes. The same temperatures and rates of flow were used. The products wanted were the unsaturated dichlorides, $C_4H_6Cl_2$, and the unsaturated monochlorides, C_4H_5Cl . The unreacted trichlorides and the dichlorides were collected mainly in the distilling flask attached to the end of the reaction tube. The monochlorides and the HCl passed on and were bubbled through water maintained near $0^\circ C$. The HCl was absorbed and the monochlorides collected above the water. The remaining gases were bubbled through a solution of bromine in CCl_4 . After one passage of the oil through the hot tube, the material in the distilling flask could be drained out and recycled. At the end of a run, the oil was collected into a single flask and distilled. For best results, the oil should be distilled as soon as possible. If allowed to stand over night, some of the wet oil will polymerize and a jelly-like mass will form on the surface.

Distillation starts at $50^\circ C$, with very little coming over below 60° . Most of the monochlorides come over between 60° to 70° with a large fraction boiling at 66° . Anything boiling below 80° was considered to be a monochloride, above 80° a dichloride. Very little comes over between 80° to 100° . Most of the dichlorides come over above 115° . Anything above 138° was considered un-

changed trichloride.

A typical run on trichloro butane is as follows: 611 g. were passed through once in three hours at 500° C. Distillation gave 53 g. of monochlorides, 169 g. of dichlorides and 242 g. of unchanged trichlorides. On the basis of the trichlorides used, this gives a yield of 26% unsaturated monochlorides and 56% unsaturated dichlorides. Some unsaturated light gases bubbled through the solution of bromine in CCl_4 . They consisted of butadiene formed from the 1, 4 dichloride present with the trichlorides, and of other light gases probably formed by the splitting of carbon linkages. No attempt was made to determine the amount of these gases, but butadiene has been identified.

Identification of Products

The unsaturated monochlorides obtained from di- and trichloro butane have practically the same boiling range. Each are collected between 50° to 80° C. with the main fraction boiling between 60° to 70° and each having a large fraction boiling around 65° to 66°.

The following data was collected on the monochlorides obtained from the trichloro butanes--boiling range 60° to 70°. An analysis for chlorine gave 40.8%-40.8%, compared to a theoretical value of 40.1% for $\text{C}_4\text{H}_5\text{Cl}$ and 39.2% for $\text{C}_4\text{H}_7\text{Cl}$. Molecular weight determinations gave values of 89-90 compared to the theoretical value of 88.5. Bromine does not seem to add quantitatively to this compound.

Bromination in glacial acetic acid gave a product with a molecular weight of 238-249, an increase of around 155 indicating one double bond. The method of Uhrig and Levin³¹ for the determination of the bromine number was tried but did not give any results. The Hanus method used in determining the iodine numbers of fats was used with the following percentage additions based on the assumption of two double bonds: 37.4, 43.7, 40.3.

Considering the unsaturated monochlorides obtained from the dichloro butanes, boiling range 60° to 70°, the percentage addition by the Hanus method based on the assumption of one double bond was 57.9%-57.4%.

The above data indicates that iodine does not add quantitatively to either of the unsaturated monochlorides, but a differentiation between the two compounds is shown, indicating at least that they are different. Other evidence points strongly to the presence of one double bond in the product obtained from dichloro butane and of two double bonds in the product obtained from trichloro butane. The index of refraction at 28° C. of these two compounds compared to the saturated compound, 2-chloro butane, are as follows:

C ₄ H ₉ Cl (saturated)	1.3970
Obtained from dichloro butane	1.4170
Obtained from trichloro butane	1.4546

An increase in the index of refraction of these compounds

indicates an increase in unsaturation. Another line of evidence which corroborates the above data is the fact that the monochloride obtained from trichloro butane polymerizes very easily while the monochloride obtained from dichloro butane is difficult to polymerize. It is known that ease of polymerization increases with unsaturation.

The above data indicates that the monochloride obtained from dichloro butane contains one double bond while the monochloride obtained from trichloro butane contains two double bonds; their formulas are, therefore, C_4H_7Cl and C_4H_5Cl , respectively.

The material obtained from the pyrolysis of trichloro butane and boiling from 100° to 138° is unsaturated dichloro butane. A fraction boiling from 115° to 130° was found to have a molecular weight of 123-119 compared to a theoretical value of 125. The presence of a double bond is indicated by the facts that it will decolorize a bromine solution of CCl_4 and by the fact that it has a high index of refraction, 1.4712 at 27° compared to 1.4480 for $C_4H_8Cl_2$ boiling range 130° to 134° . Its formula is, therefore, $C_4H_6Cl_2$.

Polymerization of Unsaturated Chloro Butanes

If the products obtained by the pyrolysis of trichloro butane are collected at the end of a run and distilled with steam, some oil will come over, the composition of which will vary from the unsaturated monochlorides to the unchanged trichlorides, and some of the original oil present will remain in the flask as a polymerized residue containing entrained water and heavy oil. As one example, 438 g. of oil were subjected to steam distillation. 260 g. of the oil came over with the steam, and the remainder had undergone polymerization and stayed in the flask.

If the same kind of oil as was subjected to steam distillation is allowed to stand overnight at room temperatures and with a little water floating on its surface, there will be formed a similar polymerized material on the surface of the oil.

The polymerized material obtained under the two conditions just described is not viscous enough to stand alone. It seems to be just a tarry mass with lots of entrained water and oil. If this mass is placed in an evaporating dish on a sand bath at 110°, there will remain after evaporation a black tarry residue. The presence of moisture in the pyrolyzed oil seems to be one of the requirements for the formation of this polymer.

Most of the studies on polymerization have been made

on unsaturated chloro butanes which have been separated by distillation into oils of a definite boiling range. The C_4H_5Cl compounds boiling below 60° are polymerized more readily than those boiling in the range 60° to 70° . If the oil boiling below 60° is placed in a stoppered test tube with just enough moisture to make the oil look cloudy, it will polymerize sufficiently in three weeks at room temperature so that it will not run when the test tube is inverted. The polymer is slightly yellow, but it is clear. This same oil in the presence of metallic sodium at room temperature will not pour after two days; in the presence of sodium peroxide or sodium sulfide it will not pour after six days.

The C_4H_5Cl compounds boiling in the range 60° to 70° will not pour after being in contact with metallic sodium at room temperature for four days. After seven days in contact with sodium peroxide or sodium sulfide at room temperature, they become a viscous polymer. If the dry oil is allowed to stand in a glass stoppered bottle it will gradually become a clear yellow color and its viscosity will increase. If this oil is placed in a sealed tube with water at 90° to 100° for two days, it becomes a very viscous polymer. Upon further, polymerization, the polymer becomes like rubber. The best rubber obtained has been made from this same oil (C_4H_5Cl , boiling range 60°

to 70° C.) by heating the dry oil in a sealed tube at 110 C. for twenty-four hours. This rubber has a strong odor at first which gradually diminishes. It is light brown in color. It is elastic and its physical properties resemble those of natural rubber.

Attempts have been made to polymerize the unsaturated dichloro butanes obtained from trichloro butane and having one double bond. Fractions boiling between 100° to 120°; 120° to 130°; and 130° to 140° have been heated several days at 110° in sealed tubes, both with and without moisture. In all cases the oils became darker in color, probably due to decomposition. The oils boiling between 100° to 120° and 120° to 130° which were heated in the presence of water showed signs of polymerization. The oil as a whole didn't become more viscous but it contained flakes of polymers. The fraction boiling from 120° to 130° showed evidences of polymerizing at room temperature upon the addition of a normal solution of NaOH. No promising results were obtained, however.

Polymerization of the unsaturated monochlorides obtained from dichloro butane and having one double bond has not met with much success. A polymer is formed in the presence of metallic sodium, but the polymer seems to form around the sodium and then greatly retards the formation of more polymer. Some polymer is formed in the presence of sodium peroxide. The dry oil can stand at

room temperature for several months without any apparent change. Samples have been heated in sealed tubes at 110° for several days, with and without water. No polymerization was noticed. The oils became very dark, probably due to decomposition.

Conclusion

Methods have been described for chlorinating n-butane. The ratio of the isomers of dichloro butane obtained by chlorinating 2-chloro butane may be altered slightly by different conditions of chlorination. Good yields of trichloro butanes can be obtained. The pyrolysis of di- and trichloro butanes has been studied and the principal products formed have been identified as to formula. Unsaturated chloro butanes have been polymerized. An artificial rubber has been prepared from the low boiling pyrolysis products of trichloro butane.

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