ACKNOWLEDGMENT

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Production of Hexachlorobutadiene

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In a continuation of chlorination-chlorinolysis studies, hexachlorobutadiene has been produced as the principal product of the chlorination of polychlorobutanes at high temperature and atmospheric pressure. Simultaneous chlorinolysis yields some carbon tetrachloride, tetrachloroethylene, hexachloroethane, and hexachlorobenzene. Starting materials were prepared from butane or chlorobutanes by photochemical chlorination. Polychlorobutanes thus produced were passed, with chlorine, through a hot tube and the products recovered. The hot tube chlorination process was studied extensively to determine optimum conditions for the production of hexachlorobutadiene. Yields in excess of 75% of this interesting chlorocarbon having conjugated double bonds may be obtained by the new process.

THE chlorination and dehydrochlorination of hexachlorobutene in the presence of various metallic chloride catalysts, such as ferric or antimony, at temperatures of 70° to 140° C. to yield hexachlorobutadiene are the subject matter of several patents (*3*, *4*).

The present investigation included the chlorination of polychlorobutanes at high temperature and atmospheric pressure in a hot tube without the employment of a catalytic agent. High yields of hexachlorobutadiene are obtained in this manner; minor proportions of carbon tetrachloride, tetrachloroethylene, and hexachloroethane were formed during the process by simultaneous and competitive chlorinolysis. Variables in the process were studied extensively to determine optimum conditions.

PREPARATION OF POLYCHLOROBUTANES

It has been shown (*2*) that a polychlorinated paraffin hydrocarbon may be produced by introduction of the hydrocarbon and chlorine through inlets maintained a relatively short distance apart into an irradiated body of liquid, preferably a body of material which is similar to the product to be produced by the chlorination reaction. In a detailed study of the process as applied to the chlorination of propane, it was found that the specific gravity of the product increased with a higher ratio of chlorine to propane, and that only small quantities of mono- and dichloropropanes were ever present in the reaction products. This procedure was applied to the preparation of polychlorobutanes for the present investigation.

The effect of various ratios of chlorine to butane on the continuous photochemical chlorination of butane was studied extensively. In general, the specific gravity of the product increased with a higher mole ratio of chlorine to butane up to a ratio of about 7 to 1. For example, with a chlorine to butane mole ratio of 6 to 1, the specific gravity of polychlorobutane product was 1.63; at a mole ratio of 7 to 1, the specific gravity was 1.68; but at a mole ratio of 8 to 1, the specific gravity was again 1.68. With the latter ratio, free chlorine was present in the exit gases. The chlorinations were generally carried out at about 80° C., as considerable chlorinolysis was found to occur at temperatures substantially above 90° C. In some instances, polychlorobutanes produced by the continuous process were chlorinated batchwise to products of higher specific gravity.

The capacity of the reactor (75 cm. × 75 mm.) (*2*) was determined at a temperature of approximately 80° C. under conditions at which substantially all of the chlorine and butane reacted. At a mole ratio of 6 chlorines to 1 butane, the capacity was 15 liters of butane and 90 liters of chlorine per hour; at a mole ratio of 7 to 1, the capacity was found to have decreased to 6 liters of butane and 42 liters of chlorine per hour.

The same photochemical chlorination technique as described for the conversion of butane to polychlorobutanes was applied successfully to butene with a substantial saving of chlorine. This is of commercial significance, as a mixture of butane and butenes is readily available from petroleum refineries.

CHLORINATION OF POLYCHLOROBUTANES

Although the reaction of chlorine and tetrachlorobutane at high temperatures and pressures has been shown to give high yields of hexachloroethane (*1*) alone or together with carbon tetrachloride, depending upon the exact conditions employed, and it has been shown that carbon tetrachloride and tetrachloroethylene (*2*) can be obtained in excellent yields by the treatment of polychloropropanes with chlorine at elevated temperatures and atmospheric pressure, application of the latter procedure to polychlorobutanes produced only small yields of these products. The principal product of the reaction between chlorine and polychlorobutanes at high temperatures and atmospheric pressure was found to be hexachlorobutadiene. Varying amounts of carbon tetrachloride, tetrachloroethylene, and hexachloroethane were produced by a competing chlorinolysis reaction, and the ratios of these chlorocarbons in the product depended upon the conditions of reaction. Small amounts of hexachlorobenzene were also produced.

APPARATUS. The production of hexachlorobutadiene was carried out in an apparatus similar to that described for the chlorinolysis of polychloropropanes (*2*).

Chlorine and polychlorobutanes were mixed at a tee and the mixture was introduced into the reactor consisting of coil made from 12-mm. Pyrex tubing and having a volume of 200 to 250 ml. The reactor was heated to 400° to 500° C. in a bath of molten sodium and potassium nitrate. The temperature of the bath was measured by a thermometer. Reaction products passed from the reactor into an air-cooled receiver and thence into a water scrubber. Unreacted chlorine and uncondensed organic products leaving the scrubber were collected in a receiver maintained at dry ice temperature. The organic products were combined and washed with a dilute sodium bicarbonate solution and dried.

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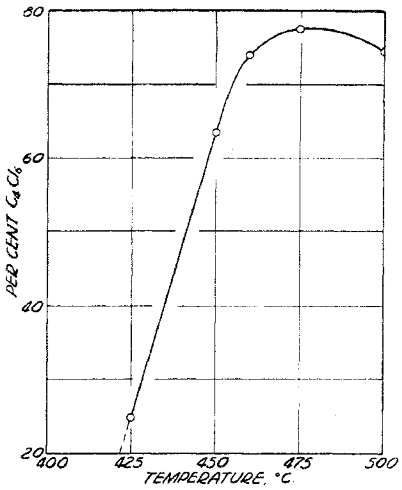

Figure 1. Effect of Temperature on Production of Hexachlorobutadiene

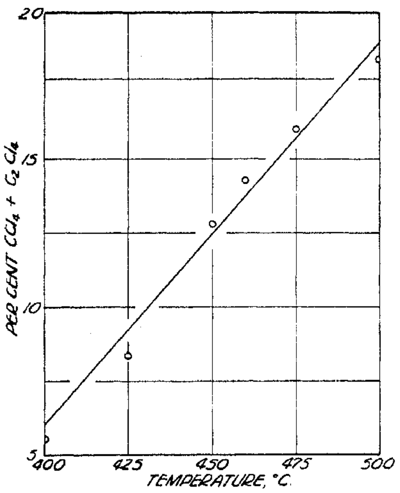

Figure 2. Effect of Temperature on Carbon-Carbon Cleavage

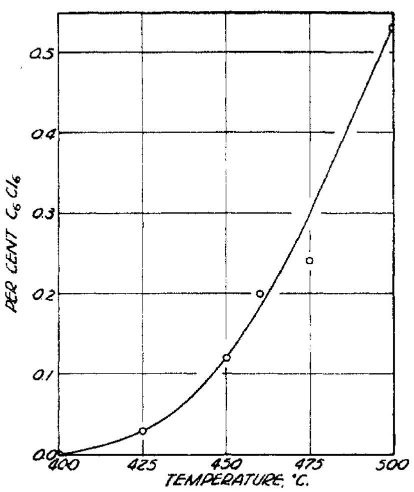

Figure 3. Effect of Temperature on Production of Hexachlorobenzene

The organic product was rectified in a 4-foot column packed with glass helices. Carbon tetrachloride and tetrachloroethylene were distilled at atmospheric pressure; hexachloroethane, if any, and hexachlorobutadiene were distilled at about 20-mm. mercury pressure. The residue was steam distilled, leaving hexachlorobenzene. Product identity was ascertained by physical constants and, in the case of hexachlorobutadiene, by chlorine analysis. Some material boiling lower than hexachlorobutadiene was detected in the rectifications, and, though not identified, was believed to consist of polychlorobutanes, polychlorobutenes, and polychlorobutadienes.

REACTION VARIABLES. Important considerations in the production of hexachlorobutadiene by reaction of polychlorobutanes and chlorine at elevated temperatures and at atmospheric pressure are temperature, exposure time, ratio of reactants, and nature of the starting polychlorobutanes. Numerous experiments were performed in an effort to study these variables. An average composition of the starting material was estimated from the specific gravity to allow correlation of data. Obviously, the polychlorobutanes were a mixture of isomers and of compounds of different chlorine content.

TEMPERATURE EFFECT. The effect of temperature was examined in the range 400° to 500° C. Polychlorobutanes having a specific gravity of 1.66, an average composition of approximately $C_4H_{3.5}Cl_{6.5}$, were prepared by the batch chlorination of polychlorobutanes obtained from the continuous chlorination process previously described (*2*). These were introduced into a reactor having a volume of 235 ml. at a rate of 2 ml. (3.32 grams) per minute. A total of 264.8 grams of polychlorobutanes was used in each experiment.

A flow of chlorine to the reactor was 70.3 liters per hour, giving a molar ratio of chlorine to polychlorobutanes of 4 to 1 at each temperature level investigated. The results (Table I) show that the amount of hexachlorobutadiene increases with an increase in temperature, producing a maximum yield at about 475° C., and then decreases at higher temperatures (Figure 1). The amount of carbon-carbon cleavage, as indicated by the production of carbon tetrachloride and tetrachloroethylene, also increased with an increase in temperature, as will be observed from an inspection of Figure 2. The production of hexachlorobenzene increased as the temperature rose (Figure 3) and above 475° C. traces of hexachloroethane were also present.

TABLE I. EFFECT OF TEMPERATURE[a]

Experiment No.	51	52	53	57	54	55
Temperature, ° C.	400	425	450	460	475	500
Exposure time, seconds	4.37	4.21	4.06	3.99	3.92	3.79
Product						
Weight, grams	232.5	241.6	261.9	256.6	264.9	272.9
CCl_4, %	3.1	5.0	6.3	6.4	6.6	6.8
C_2Cl_4, %	2.4	3.3	6.5	7.9	9.4	11.6
C_2Cl_6, %	...	...	...	...	Trace	Trace
C_4Cl_6, %	...	24.8	62.2	74.1	77.1	74.5
Material boiling below C_4Cl_6, %	55.6	41.9	15.6	7.5	2.2	2.1
Residue, %	38.1	23.1	8.1	3.5	3.7	2.8
C_6Cl_6, %	...	0.03	0.12	0.2	0.24	0.53

[a] Reactor volume was 235 ml.; specific gravity of the polychlorobutanes was 1.659; mole ratio of chlorine to polychlorobutanes was 4 to 1.

TABLE II. EFFECT OF EXPOSURE TIME[a]

Experiment No.	61	56	57	58	59
Polychlorobutane flow, ml./min.	0.5	1	2	3	4
Chlorine flow, liters/hour	17.6	35.2	70.5	105.6	140.8
Mole ratio, chlorine: polychlorobutanes	4	4	4	4	4
Exposure time, seconds	15.95	7.98	3.99	2.66	2.00
Product					
Weight, grams	266.5	263.3	256.6	257.1	248.8
CCl_4, %	5.7	5.7	6.4	6.5	6.0
C_2Cl_4, %	9.9	9.3	7.9	7.2	5.8
C_2Cl_6, %	Trace	Trace	...	...	...
C_4Cl_6, %	74.6	76.2	74.1	55.6	44.6
Material boiling below C_4Cl_6, %	3.3	3.2	7.5	24.4	32.7
Residue, %	3.3	4.6	3.3	5.4	8.6
C_6Cl_6, %	0.62	0.42	0.20	0.15	0.10

[a] Volume of reactor was 235 ml.

EXPOSURE TIME. The effect of exposure time was studied by varying the feed rate of polychlorobutanes to a reactor having a volume of 235 ml. In each experiment of the series, 265.4 grams of polychlorobutanes were employed, of specific gravity 1.66 and approximate composition $C_4H_{3.5}Cl_{6.5}$, which had been prepared by batch chlorination of polychlorobutanes from the continuous process. The temperature of the reactor bath was maintained at 460° C. during all runs in the series, the data for which were summarized in Table II. An exposure time of materially less than 4 seconds resulted in considerably reduced yields of hexachlorobutadiene (Figure 4), while an increase of exposure time to between about 4 and 16 seconds effected no appreciable increase. Yields of hexachlorobutadiene were actually decreased somewhat by the longer exposure times. Conversely, hexachlorobenzene (Figure 5) and products resulting from carbon-carbon cleavage (Figure 6) showed a decided increase with an increase in exposure time.

RATIO OF CHLORINE TO POLYCHLOROBUTANES. Polychlorobutanes having a specific gravity of about 1.68, produced by the continuous chlorination of butane, were passed together with chlorine into the reactor at 460° C. The results are given in Table

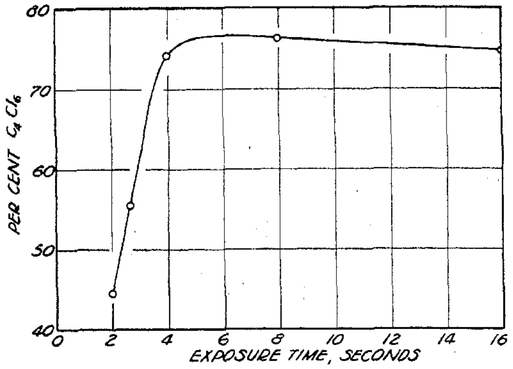

Figure 4. Effect of Exposure Time on Production of Hexachlorobutadiene

III. Exposure times for the three experiments vary, but all are greater than the critical exposure time of about 4 seconds. An increase in the ratio of chlorine to polychlorobutanes from 2.3 to 4.0 increased the yield of hexachlorobutadiene (Figure 7) as well as the amount of cleavage of carbon-carbon bonds. Increase in the yield of hexachlorobutadiene per increment increase in the ratio of chlorine to polychlorobutanes became smaller as a ratio of 4 to 1 was approached.

Table III. Effect of Chlorine to Polychlorobutane Ratio

Experiment No.	14	23	17
Volume of reactor, ml.	200	250	200
Polychlorobutanes, grams	252.6	250.4	168.4
Flow, ml./min.	2	2	1
Chlorine flow, liters/hour	38.1	56.7	33.7
Mole ratio, chlorine: polychlorobutanes	2.3	3.2	4.0
Exposure time, seconds	5.43	5.02	7.08
Product			
Weight, grams	240.1	236.8	158.2
CCl_4, %	5.4	7.2	10.3
C_2Cl_4, %	8.9	7.8	13.0
C_4Cl_6, %	55.2	63.4	64.2
Material boiling below C_4Cl_6, %	12.8	10.0	3.8
Residue, %	7.2	7.2	6.2

Similar experiments in which the chlorine was replaced by nitrogen gave only traces of the usual products. However, when polychlorobutanes of higher chlorine content (specific gravity 1.816) were used, all the usual products of the reaction were isolated, though in smaller amount.

Nature of Starting Material. The effects of the method of preparing the starting polychlorobutanes and of the specific gravity of the starting material upon the products of the high temperature chlorination were investigated in several experiments. Under similar reaction conditions, polychlorobutanes chlorinated batchwise gave slightly better yields of hexachlorobutadiene and somewhat less carbon-carbon cleavage than polychlorobutanes of comparable chlorine content prepared by continuous chlorination. A consideration of materials prepared by the same method of chlorination showed those of higher chlorine content to give increased quantities of carbon-carbon cleavage products. These data are presented in Table IV.

Table IV. Effect of Nature of Starting Material

Experiment No.	25	26	57	34	36
Volume of reactor, ml.	250	250	235	250	250
Polychlorobutanes					
Specific gravity	1.602	1.601	1.659	1.681	1.693
Weight, grams	240.3	216.1	265.4	269.0	270.9
Flow, ml./min.	2	2	2	2	2
Chlorine flow, liters/hour	54.3	54.3	70.5	62.5	59.5
Mole ratio, chlorine: polychlorobutanes	2.6	2.6	4.0	3.7	3.7
Temperature, ° C.	460	460	460	461	460
Exposure time, seconds	4.97	4.97	3.99	4.70	4.88
Product					
Weight, grams	...	209.4	256.6	245.9	254.1
CCl_4, %	4.5		6.4	9.1	10.9
C_2Cl_4, %	4.8	3.3	7.9	8.5	10.0
C_4Cl_6, %	53.2	57.4	74.1	66.6	65.2
Material boiling below C_4Cl_6, %	25.7	21.0	7.5	8.7	7.1
Residue, %	8.1	7.1	3.3	4.8	4.0
C_6Cl_6, %	...	...	0.20	0.39	0.59

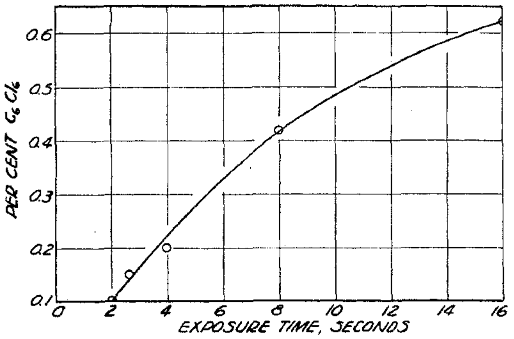

Figure 5. Effect of Exposure Time on Production of Hexachlorobenzene

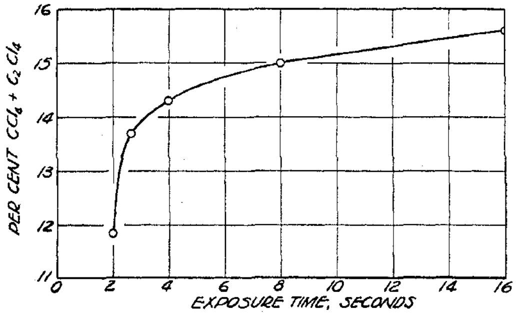

Figure 6. Effect of Exposure Time on Carbon-Carbon Cleavage

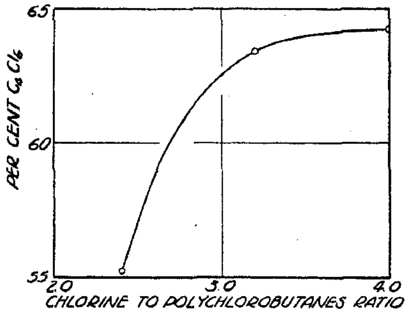

Figure 7. Effect of Ratio of Chlorine to Polychlorobutane on Production of Hexachlorobutadiene

PROPERTIES OF HEXACHLOROBUTADIENE

Hexachlorobutadiene is a high boiling, nonflammable chlorocarbon having a wide liquid range. The compound is extremely resistant to hydrolysis, even in the presence of alkali. For example, equal volumes of hexachlorobutadiene and a dilute solution of sodium bicarbonate, when heated at about 100° C. with vigorous stirring in the presence of iron, were found after 4 hours to produce a solution containing less than 0.006 mg. of chloride ion per gram of hexachlorobutadiene. Hexachlorobutadiene is insoluble in water, its solubility at 20° C. being only 0.0005%.

Further chlorination is resisted by hexachlorobutadiene. Attempts to chlorinate hexachlorobutadiene, when sealed in Carius tubes and under irradiation at temperatures from −70° to +75° C., to octachlorobutene or decachlorobutane were unsuccessful. Chlorinolysis occurred at temperatures above about 25° C., yielding hexachloroethane. Hexachlorobutadiene gave no reaction with sulfuryl chloride in the presence of benzoyl peroxide.

Hexachlorobutadiene is a colorless liquid of faint turpentinelike, odor having the following physical constants: melting point −21° C.; boiling point (760 mm.), 215° C.; d_4^{20} 1.6820 grams per ml.; and n_D^{20} 1.5542. The viscosity of hexachlorobutadiene is 2.446 centipoises or 1.479 centistokes at 37.8° C. and 1.131 centipoises or 0.724 centistokes at 98.9° C.

Hexachlorobutadiene is an excellent solvent for many organic substances. It has the distinct advantage over the common chlorocarbon solvents of having a low vapor pressure and is applicable as an agent in the extraction of organic materials from water, as a high temperature degreasing agent, as a hydraulic fluid, and as a special solvent.

CONCLUSIONS

Two competing reactions occur in the high temperature atmospheric pressure chlorination of polychlorobutanes: (1) formation of hexachlorobutadiene and (2) chlorinolysis to carbon tetrachloride, tetrachloroethylene, and hexachloroethane. The optimum temperature for the production of hexachlorobutadiene was found to be about 475° C. Exposure periods of 4 to 8 seconds gave the highest yields of hexachlorobutadiene. The yield of hexachlorobutadiene was greater at a 4.0 to 1 ratio of chlorine to polychlorobutanes than at lower ratios. Best yields of hexachlorobutadiene were obtained by using polychlorobutanes having a specific gravity of about 1.66. The chlorinolysis reaction was favored by increases in temperature, exposure time, ratio of chlorine to polychlorobutanes, or in the specific gravity of starting polychlorobutanes.

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CHARACTERISTICS OF REINFORCING FURNACE BLACKS

Processing Shrinkage

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Extrusion shrinkage measurements of GR-S–carbon black mixtures are useful for classifying the various types of furnace blacks in terms of their degree of structure. A processing shrinkage index has been defined which gives a numerical rating of carbon black structure. Standard GR-S has been shown to be a more sensitive medium than natural rubber for characterizing the processing properties of furnace type carbon blacks.

A MAJOR technical development in the rubber industry has been the recent introduction of furnace blacks possessing rubber reinforcing properties in the range of channel blacks. The literature on the subject of reinforcing furnace blacks is rapidly expanding (*1, 4, 6, 11, 12, 17–20*) to satisfy the need for information on the compounding and rubber properties of these new products.

Types of reinforcing furnace blacks are available which will duplicate closely the usual rubber properties observed with channel blacks in vulcanized stocks. However, because of the flexibility of operation and the different types of raw material adaptable to the continuous furnace process it is also possible to produce grades of reinforcing furnace blacks which differ markedly from channel blacks in rubber properties. The range of rubber stiffness and hardness obtainable with reinforcing grades of furnace blacks is much greater than with channel blacks, and although final approval of a grade of black for a particular application is based on service testing, the useful range of rubber product quality has been broadened by the introduction of new varieties of furnace blacks.

Processing characteristics of carbon blacks may be described as the relative workability factors of rubber stocks in the sequence of operations preceding the completed manufacture of cured rubber articles. In those compounds where carbon black is a substantial component of the stock it is to be expected that the properties of the black will exert a major influence on processing.

The work reported here is concerned with the effect of carbon black properties on the forming step of semifinished stocks and includes a study of the processing shrinkage properties of carbon black loaded stocks.

STRUCTURE IN CARBON BLACKS

Whereas the processing characteristics of channel blacks bear a simple relation to particle size and are the basis for their present classification in the rubber industry, the processing properties of furnace blacks cannot be correlated similarly with the same degree of fineness. It has been necessary to introduce the concept of "structure" to explain such anomalous properties as the low processing shrinkage and the smooth surface appearance of extruded and calendered stocks observed when certain grades of reinforcing furnace blacks are used. Although these effects are particularly noticeable with GR-S they can be observed also, to a lesser degree, with natural rubber. In the cured vulcanizates structure blacks are characterized by high modulus and hardness, low breaking elongations, and high electrical conductivity.