acetylation of 2,3-butylene glycol with glacial acetic acid (17), would be removed at only one point in the over-all process; the MVC and crotyl acetate intermediates would be recovered for repyrolysis with diacetate, uncontaminated with the nonbutadieneyielding MEK enol-acetate; and the distillation of acetic acid in process would be limited to that used as excess during the esterification. The deposition of tars in the esterification column, and the highly complicated mixture of materials undergoing reaction in this column would, however, make it difficult to maintain and control the continuous esterification operation. Although this method could undoubtedly be used for batch esterification, the advantages of the continuous process using purified acetic acid are obvious. Because of these factors, this method was not explored in the pilot-plant studies.

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PILOT-PLANT CONVERSION of 2,3-BUTYLENE GLYCOL DIACETATE to 1,3-BUTADIENE

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ABORATORY investigations (2) on a process for the manufacture of 1,3-butadiene from 2,3-butylene glycol by pyrolysis of the diacetate resulted in development of a small-scale pilotplant pyrolysis unit; in this apparatus the effects of various factors, such as time, temperature, and pressure could be investigated, and optimum conditions for the highest yields and byproduct recoveries could be determined. Because of critical material shortages, the design was the simplest possible which would serve to determine data for larger-scale design. The findings of this research were used as a basis for operation in the 2000-pound-per-day pilot plant of Joseph E. Seagram & Sons, Inc.

The pilot-plant pyrolysis unit (Figure 1) consisted of a gasheated lead bath in which interchangeable pyrolysis coils, having production capacities of 20 to 100 pounds of butadiene per day, could be immersed. The glycol diacetate to be pyrolyzed was pumped from a weigh tank by a proportioning pump to a vaporizer which was connected to the inlet of the pyrolysis coil in the lead bath. The outlet of the pyrolysis coil was connected through a 3-foot section of 1/2-inch I.P.S. (iron pipe size) pipe to the base of a jacketed column where the butadiene was separated from

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condensed acetic acid and other liquid pyrolysis products. These pyrolysis liquors passed through a U-trap at the base of the column, and were collected in a tared receiver mounted on a scale. The butadiene and small amounts of other gaseous products from the head of the butadiene separating column were washed with water in a small scrubbing tower to remove traces of entrained acetic acid. The gases then passed through a tower packed with calcium chloride to remove moisture. The dry gases were picked up by a compressor, through a pressure control valve, and the butadiene, compressed to 38-40 pounds per square inch, was condensed and collected in a weigh tank. The gaseous by-products, not condensable at room temperature under 38-40 pounds per square inch, were vented from the compressor system by a pressure control valve at the top of a refrigerated reflux condenser which was connected into the line carrying butadiene to the weigh tank. The weigh tank was vented to this condenser to prevent trapping of noncondensable gases in the tank. The volume of noncondensable gases was measured by a wet test meter. Samples of the vent gases, butadiene, pyrolysis liquors, and glycol diacetate feed were taken for analyses during each run. All parts of this unit which came into contact with liquid, or gaseous, acetic acid were constructed of stainless steel.

Pilot-plant studies of the process for producing 1,3butadiene from 2,3-butylene glycol diacetate by pyrolysis have shown that an 88% yield can be obtained. The process consists in pyrolyzing the diacetate at 595° C. to obtain an 83% conversion to 99+% pure butadiene. The intermediate butenol acetates are separated from the acetic acid of the pyrolysis liquors and repyrolyzed to obtain the additional 5% of butadiene. Approximately 3% of useful by-products are obtained. These consist of methyl ethyl ketone, methyl ethyl ketone enol-acetate (2-acetoxy-2-

Thermocouples were inserted in the outlet of the vaporizer, in the lead bath, in the outlet of the pyrolysis coil, in the line connecting this coil to the column, and in the base and head of this column. The thermocouple in the vapor stream at the outlet of the pyrolysis coil was connected to an indicating temperature controller which controlled the lead-bath heating mechanism. This arrangement served to control the outlet pyrolysis vapor temperatures within $\pm 2^{\circ}$ C. The pyrolysis temperatures referred to later are those measured by this thermocouple.

Pressure gages were installed at the inlet of the vaporizer, between the vaporizer and the pyrolysis coil, between the pyrolysis coil and the butadiene stripping column, and between the drying tower and the butadiene compressor.

This pilot plant was sufficiently versatile to permit the study of pyrolysis conditions over a wide range: production rates up to 100 pounds of butadiene per day, temperatures up to 700 $^{\circ}$ C., contact times as low as 0.1 second, and pressures between several inches vacuum and 300 pounds per square inch.



The contact times referred to in these studies were calculated in the same manner as those reported in the laboratory work (2), i.e., by the empirical formula:

Contact time (sec.) =
$$\frac{\text{(vol. of tubes in ml.) 60}}{\left(\frac{T}{273}\right)\left(\frac{22,400}{\text{mol. wt.}}\right) (\text{g./min. feed})}$$

In the coil-type pyrolysis chamber it was not possible to measure the gas temperatures in the various parts of the coil or to predict the exact volume of the reaction zone. A portion of the coil necessarily served to raise the temperature of the entering vapor toreaction temperature, and obviously the true reaction zone volume was not the total coil volume. Since the total coil volume and the temperature of the gases at the coil outlet were the only definitely determinable factors, all contact time calculations were based on these values. The contact times indicate the residence time in the total coil length, assuming a constant temperature throughout. That these contact time values are relative to each other at each







Figure 2. Effect of Temperature on Conversion-Contact Time Data (Jacketed Pipe Cooling System)

temperature studied is indicated by the uniformity of results obtained in two coils of different lengths constructed of different sizes of pipe. In both of these coils the peaks of the conversioncontact time curves, at a gas outlet temperature of 595° C., were found to be at about the same contact time. This indicates that the portion of the coil required to raise the entering vapors to reaction temperature is proportional to the total coil volume in both cases.

The 2,3-butylene glycol diacetate used in the pilot-plant studies was prepared by large-scale batch esterification of the glycol (3), and was all 99-100% pure.

PYROLYSIS STUDIES

Orienting experiments were conducted in a pyrolysis coil constructed from a 27-foot length of 1/s-inch I.P.S. stainless steel (18-8-Cb) pipe which had a butadiene production capacity of about 20 pounds per day. A series of relatively short runs served to establish conversion-contact time data at temperatures varying from 575° to 625° C.

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TABLE I.	DIACE	LANT PY	ROLYSES	of 2,3-1 ⁹ , and 60	J5° C.	GLYCOL
Contact Time, Sec.	Temp., °C.	Buta- diene Yield, %	Unsatd. Acetate Yield, %	Hydro- carbon Yield, %	Acetic Acid Re- covery, %	Weight Recov- ery, %
$1.57 \\ 1.49 \\ 1.33$	585 585 585	$82.7 \\ 82.6 \\ 81.5$	$7.1 \\ 6.8 \\ 7.2$		98.1 97.4 99.6	99.0 98.6 99.0
1.44 1.36 1.25 1.16 1.04 0.891	595 595 595 595 595 595 595	80.2 80.1 81.7 83.9 82.6 83.2	5.0 5.8 6.0 7.0 5.8 8.4	$12.9 \\ 11.9 \\ 9.8 \\ 7.6 \\ 10.1 \\ 6.3$	100.2 99.4 99.3 100.0 100.2 99.9	99.9 99.2 99.0 99.9 99.8 99.8
$0.912 \\ 0.792 \\ 0.681$	605 605 605	$82.2 \\ 82.4 \\ 81.4$	$ \begin{array}{c} 6.1 \\ 7.0 \\ 7.3 \end{array} $	$10.0 \\ 8.4 \\ 9.1$	99.4 99.4 98.9	99.6 99.7 99.6

Data at 585°, 595°, and 605° C. are given in Table I and plotted in Figure 2. These data again demonstrate (2) that the pyrolysis reaction of 2,3-butylene glycol diacetate to butadiene is very sensitive regarding tempera-

to butadiene is very sensitive regarding temperature and contact time. Maximum one-pass conversions were obtained at 595° C. at a contact time of 1.04 seconds. At this optimum contact time, temperatures varying $\pm 10^{\circ}$ C. from the optimum of 595° C. give noticeably decreased conversions to butadiene. At 585° and 605° C., butadiene yields of 81.1 and 77.1%, respectively, are obtained.

Several long runs lasting 30 to 48 hours were made to establish yield, quality, and material recovery data. At contact times ranging from 0.97 to 1.02 seconds, these runs gave an average yield of 82.1% of 99% pure butadiene. The over-all weight recovery averaged 99.8, and acetic acid recovery was also 99.8%. An average of 0.62% of the total weight of glycol diacetate pyrolyzed was converted to noncondensable gases. These runs served to confirm the yields and quality of the butadiene and the high acetic acid and weight recoveries that had been indicated in the shorter runs.

COOLING OF PYROLYSIS VAPORS. For these runs, a waterjacketed 1/2-inch I.P.S. pipe served to cool the pyrolysis vapors going to the butadiene stripping column. Approximately 0.3 second was required to cool the pyrolysis vapors from 595° to 118° C. During this interval some butadiene dimerized (the rate of this reaction being quite rapid at elevated temperatures), and some of the methyl vinyl carbinol and crotyl acetates in the pyrolysis liquor pyrolyzed to butadiene. This loss of butadiene through dimerization, as well as the pyrolysis of the butadieneyielding acetates under nonoptimum conditions, was undesirable. To obtain the highest yields of butadiene, the pyrolysis and polymerization reactions should be stopped immediately as the vapors leave the pyrolysis coil. A spray-quench system, shown in Figures 1 and 3, was therefore built into the pyrolysis vapor line, adjacent to the pyrolysis coil outlet. Cooled pyrolysis liquors were pumped by a proportioning pump through the spray housing into the pyrolysis vapor stream,

A larger pyrolysis coil, made from 45 feet of $\frac{1}{4}$ -inch I.P.S. high-chrome steel pipe and having a capacity of 100 pounds of butadiene per day, was then installed. Data obtained in this pyrolysis unit at the optimum temperature of 595°C. are given in Table II and are plotted as the lower curve in Figure 4. About 0.5% of glycol diacetate remained unreacted in all runs.

Table II shows a substantial reduction in hydrocarbon formation over the earlier pilot-plant results shown in Table I. The percentage retention of methyl vinyl carbinol and crotyl acetates increased correspondingly. The most striking feature of the results was that approximately the same conversion to butadiene could be obtained under optimum contact time and temperature conditions, with or without the spray-quench system, but with this system in operation the pyrolysis liquors contained greater amounts of the butadiene-yielding acetates and lesser amounts of hydrocarbons. This fact indicates that the breakdown of these acetates and the hydrocarbon formation substantially balanced each other during the time required to cool the pyrolysis vapors in the earlier experiments.

Figure 4 indicates that the use of spray quenching permits closer control of the pyrolysis reaction and greater reproducibility of results.

OTHER FACTORS AFFECTING BUTADIENE YIELD. A number of other factors were investigated during the course of the pilotplant pyrolysis studies. The most significant of these follow:

The quality of the diacetate is of particular importance (2). The presence of glycol monoacetate is undesirable since this material is decomposed to products other than butadiene and acetic acid on pyrolysis, resulting in a lower yield of glycol to butadiene. Traces of acetic anhydride in the diacetate adversely affected the butadiene yield. Acetic acid had no harmful effect. Traces of

TABLE II. PILOT-PLANT PYROLYSES OF 2,3-BUTYLENE GLYCOL DIACETATE AT 595° C. (USING SPRAY-QUENCH SYSTEM)

Contact Time, Sec.	Buta- diene Yield, %	<u>Unsatd</u> Total	. Acetate MEK ^a acetate	Yield, % MVC acetate	Hydro- carbon Yield, %	Free MEK Yield, %	Conversion to Noncon- densable Gases, Wt. %	Cumu- lative Yield ^a , %
0.92 1.01 1.02 1.027 1.06 1.07 1.08 1.114	$\begin{array}{c} 75.9\\ 81.62\\ 82.09\\ 82.6\\ 82.75\\ 82.90\\ 82.84\\ 81.8 \end{array}$	$14.23 \\ 10.46 \\ 10.72 \\ 11.05 \\ 10.31 \\ 12.37 \\ 9.79 \\ 11.00 \\$	5.44 4.47 5.11 4.30 4.82 4.54 4.68	$\begin{array}{c} 8.79 \\ 5.99 \\ 6.00 \\ 5.94 \\ 6.01 \\ 7.55 \\ 5.25 \\ 6.26 \end{array}$	1.28 1.97 1.44 1.22 3.12 0.22 0.36 0.63	$1.28 \\ 1.62 \\ 1.73 \\ 1.35 \\ 1.97 \\ 1.41 \\ 1.70 \\ 1.41$	0.58 0.59 0.60 0.57 0.55 0.59 0.64	83.37 86.72 87.70 87:65 87.86 89.32 87.81 87.12
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^a Approximately 30% methyl acetyl acetone.

September, 1945



Figure 3. Pyrolysis Furnace in Butadiene Pilot Plant, Showing Preheater, Gas Heating System, Spray-Quench System, and Butadiene Stripping Column

copper salts dissolved in the diacetate had no harmful effects on the butadiene yield and quality. There were no detectable differences between the results obtained from diacetates prepared from the meso- or levorotatory glycols.

The effect of pressure in the pyrolysis system was investigated. Pressure up to 14 pounds per square inch had no noticeable effect on butadiene yields. At 80 pounds per square inch the butadiene yield was markedly reduced, with a corresponding increase in hydrocarbon formation. Slightly reduced pressures, 5–6 inches of vacuum, showed no measurable differences as compared with atmospheric pressures.

Some data on pressure drops across the pyrolysis coil were determined. With the 27-foot coil of 1/s-inch I.P.S. pipe, the pressure differential varied from 1.2 to 1.8 pounds per square inch over several months of operation. With the 45-foot coil of 1/sinch I.P.S. pipe, the pressure drop was 7.0 to 11.8 pounds per square inch. In both cases, the pressure differential increased slightly over long periods of operation. This was probably caused by gradual deposition of carbon, although its amount was too small to be measured. In either case the pressure differences were not of sufficient magnitude to cause significant variations in yield.

QUALITY OF THE BUTADIENE. The butadiene obtained in all of these pilot-plant pyrolysis runs was of excellent quality, 99 to 100% pure by analysis. Tests by The Goodyear Tire and Rubber Company showed that it was satisfactory for synthetic rubber manufacture after simple distillation to remove small amounts of dimer and antioxidants which had been added.

SEPARATION OF COMPONENTS OF THE PYROLYSIS LIQUORS

Laboratory investigations (2) of the pyrolysis liquors served to establish which of the pyrolytic intermediates and by-products were capable of yielding butadiene on repyrolysis so that, by examination of the analytical data, it was possible to predict the potential yield of butadiene from the original diacetate. Pilotplant data indicated that the highest cumulative yields were obtained under conditions giving the highest first-pass yields. Examination of numerous pyrolysis data from runs under these conditions showed that the formation of nonbutadiene-yielding byproducts averaged 10 to 12%. Therefore, the indicated maximum butadiene yield was 88 to 90% of theoretical.

The best means of obtaining the additional butadiene, available on repyrolysis of the intermediates in the pyrolysis liquors, was considered from several angles. Since these liquors consisted of about 85% acetic acid, repyrolysis would involve the handling of large volumes of material in order to produce an additional 5 to 6% of butadiene. A pyrolysis chamber nearly equal in size to that used for the initial diacetate pyrolysis would be required if this second stage were to be run separately. Direct recycling of the total liquors to the diacetate feed was not desirable for two reasons: First, the pyrolysis chamber would have to be much larger to accommodate the greater volume of materials handled. Second, pyrolysis of the nonbutadiene-yielding components had shown that these materials gave some breakdown products which were not readily separable from butadiene. For these reasons it seemed desirable to separate the intermediates from the bulk of the acetic acid and then repyrolyze these materials in an auxiliary unit.

BATCH SEPARATION. It had been found (2) that the intermediates, by-products, and acetic acid of the pyrolysis liquors could be separated if some water, not to exceed 25% of their

weight, was added to these liquors, and this mixture was distilled. Practically all of the nonacetic acid components boiling below 150° C. could be removed as water azeotropes. Under the conditions of batch operation, in which the water was added to the liquors and distillation carried to a point where the distillate no longer separated into two layers, the still residues consisted of about 85% acetic acid, 3-5% of the high boiling materials, and 10-12% water. The distillate from this operation separated into water and oil layers. The oil layer was dried by distillation of its azeotrope to a decanter which continuously removed water from the system. The dried oil comprised a mixture of free methyl ethyl ketone, methyl ethyl ketone enol-acetate, methyl vinyl



Figure 4. Effect of Contact Time on Butadiene Yield at 595° C. (Spray-quench cooling system)

carbinol acetate, crotyl acetate, steam volatile hydrocarbons, and less than 10% acetic acid.

Under batch stripping conditions, about 20% of the methyl ethyl ketone enolacetate present in the original pyrolysis liquors was hydrolyzed. The bulk of the butadiene - yielding acetates was recovered unchanged. This method was used for the recovery of the unsaturated acetates in most of the pilotplant studies. The acetic acid residue was dehydrated by a batch-operated

entrainer system, and then used for the esterification of glycol by the batch method described in another paper (3).

Laboratory distillations of the acetic acid residue from the stripping operation showed that it was readily fractionated into dilute acetic acid, a main cut of 98-100% acetic acid, and a residue of high-boiling materials.

On the basis of these results it appeared that the stripping operation provided a means for both the separation of repyrolyzable acetates from the acetic acid and the production of a readily rectifiable acetic acid. In addition to accomplishing the desired separation of the pyrolysis liquors, the stripping operation was found to be adaptable to continuous operation. This was confirmed in both the laboratory and the pilot plant.

CONTINUOUS SEPARATION. For pilot plant operations a copper column 6 inches in diameter and 5 feet high was constructed. It contained four bubble-cap plates at the top and sixteen perforated screen-covered plates. All plates were spaced about 3 inches apart. The pyrolysis liquors were pumped through a heat exchanger, which raised their temperature to 95-100° C., and were then introduced into the middle plate of the column. The decanter, attached to the condenser drain at the head of the column, was filled with water, and sufficient water was introduced into the column itself to fill the four bubble-cap plates at the top. The column was mounted on a 30-gallon kettle equipped with steam coils. In operation the liquors distilling up the column contacted the water in the upper section where the water-oil azeotropes were fractionated from the acetic acid. The distillate was condensed and run to a decanter which continuously returned the water layer to the top plate of the column and drained the oil layer to a receiver. The stripped acetic acid was removed from the base receiver. Table III shows the results obtained on a typical run in the pilot plant column.

TABLE III.	Separation of Acetates from Pyrolysis Liquors
	BY AZEOTROPIC STRIPPING

	Wt. of Co			
Component	Pyrolysis liquor feed	Unsatd. acetate fraction	Acetic acid residues	Re- covery, %
Acetic acid- Unsatd. acetates Free methyl ethyl	$\begin{array}{r} 36.35 \\ 4.96 \end{array}$	$\begin{array}{c} 0.33 \\ 4.023 \end{array}$	$\substack{\textbf{36.2}\\\textbf{0.80}}$	100.4 96.8
ketone Diacetate	$\begin{array}{c} 0.499 \\ 0.256 \end{array}$	$\substack{\textbf{0.487}\\\textbf{0.041}}$	$\substack{0.00\\0.215}$	$\begin{array}{c} 97.6\\100.0\end{array}$

These results indicate about a 3% loss of the unsaturated acetates during the stripping operation. The high-boiling material left in the stripped acetic acid consisted largely of methyl acetyl acetone. The material removed during the stripping included essentially all of the butadiene-yielding unsaturated acetates.

The pilot-plant column was not efficient enough to produce an anhydrous acetic acid solution of high-boiling materials as the base product. Fractionation of this material through another column gave a first cut of dilute acetic acid and a main fraction of 98–100% acetic acid. All other materials in this mixture boiled above 150° C.

PYROLYSIS OF UNSATURATED ACETATES

Separation of the butadiene-yielding methyl vinyl carbinol and crotyl acetates from the methyl ethyl ketone enol-acetate by fractional distillation of the mixture separated from the diacetate pyrolysis liquors had been found impractical (2). It was desirable, however, to distill the mixed acetates before repyrolysis in order to remove components boiling above 140° C. which caused coke deposition in the pyrolysis chamber.

The pyrolysis of these mixed unsaturated acetates was studied in both the laboratory and pilot plant. In general, the temperature-contact time relations were found to be less critical than for the diacetate pyrolysis, and a much higher proportion of noncondensable gases was produced. Pyrolyses conducted at 595° C. and a contact time of 0.6 second, followed by two recycles of the liquors, resulted in an 84.4% conversion of the methyl vinyl carbinol-crotyl acetates fraction to butadiene and an 87% acetic acid recovery.

By applying the conversion value of 84.4% to the methyl vinyl carbinol-crotyl acetates, produced in the diacetate pyrolyses shown in Table II, the over-all butadiene yields may be calculated. These cumulative yields (last column) average about 88% for these runs in which the diacetate was pyrolyzed under optimum conditions. The upper curve in Figure 4 illustrates these cumulative yields.

The butadiene produced by pyrolysis of the mixed unsaturated acetates was only 85% pure. Since the effect of these impurities on the polymerization characteristics of the butadiene was not known, the pilot plant pyrolysis of these recovered acetates was conducted as a separate operation. Although the amount of butadiene thus obtained represents only 5-6% of the total from the initial diacetate, it seemed desirable to purify it separately, rather than to contaminate the 99+% pure product from the diacetate pyrolysis. Fractional distillation gave a main cut of over 90% purity so that the purity of the composite butadiene would be reduced by less than 0.5%.

The 13% loss of acetic acid, incurred during the pyrolysis of the recovered acetates, does not seriously affect the acid recovery on the basis of the over-all process. Since only 3% of the total acetic acid is involved in this operation, the loss amounts to 0.4% of that in process.

RECOVERY OF BY-PRODUCTS FROM HIGH-BOILING RESIDUES

The high-boiling residues left on distillation of the stripped acetic acid and those from the rectification of the acetate mixture from the stripping operation consisted mainly of polymeric tars, methyl acetyl acetone, and small amounts of unpyrolyzed glycol diacetate. The methyl acetyl acetone and the diacetate may be separated from the tars by steam stripping the residues, or the greater portion may be recovered by distillation under reduced pressure. The amount of diacetate recoverable from these residues is so small that it is doubtful if a recovery operation is justified. The methyl acetyl acetone is more readily recoverable and may be of value, although its utility has not been established. Both of these materials may be hydrolyzed with alkali and the acetic acid recovered from the hydrolysis mixture on acidification. Under these conditions methyl acetyl acetone yields acetic acid and methyl ethyl ketone. Unless more useful outlets can be found for methyl acetyl acetone, hydrolysis for purposes of acetic acid recovery may be the most economical means of disposal. The small amount of glycol diacetate may be directly recovered and returned to pyrolysis, or it may be hydrolyzed and the acidified hydrolysis residue combined with fermentation beers prior to concentration and glycol recovery.

All of the important steps of the pyrolysis and recovery operations discussed here have been conducted on a semiplant scale in standard equipment by the research and pilot-plant engineering staff of Joseph E. Seagram & Sons, Inc. (1). These operations gave satisfactory results, and there is every indication that the yields and recoveries obtained in the small scale plant can be duplicated in plant-size equipment.

PROPOSED CONTINUOUS PROCESS

On the basis of the results presented in this and the paper on esterification (3), the over-all process for butadiene from 2,3-butylene glycol may be summarized as follows:

The glycol is acetylated in a column which functions as a continuous countercurrent reactor. The bulk of the excess of the acetic acid used, of the water formed, and of the methyl ethyl ketone produced during this operation pass as vapors to a de-

TABLE IV. MATERIALS BALANCE FOR CONVERSION OF 2,3-BUTYLENE GLYCOL TO 1,3-BUTADIENE

	Pounds	Mol. Wt.	Moles	Moles per Mole	Parts per Part	% Yield Based on Glycol	% Re- covered as Such
Materials charged							
2.3-Butylene glycol	195.16	90.1	2.166	1.00	1.00		
Acetic acid	519 84	60.0	8 664	4 00	2 665		
Sulfuric acid	3.46	98 i	0.0358	0.0163	0.0077		
Products and recoveries	5						
1.3-Butadiene	100 D	54 08	7 849	0 854	0 512	85 40	
Acetic acid	517 39	60 00	8 623	3 98	2 651		99.5
Methyl ethyl ketone	17 54	72 1	0 244	0 1124	0 0898	11 24	00.0
Hydroearbona and			V. # X X	···	0.0000	11.4.1	
ters	2 20	(54 1).	0.0407	0.0188	0.0113	1 88	
2 2 Butulane given	4.40	(04.174	0.0407	0.0100	0.0110	1.00	
(as dinestate)	1 89	174 3	0.0105	0.005	0.005		0.50
Noncondensable	1.00	114.1	0.0100	0.000	0.000		0.00
roncontensable	0.07				0.00794		
28868	4.86				0.00/0		

hydration column in which the water and methyl ethyl ketone are removed by an entrainer system. The methyl ethyl ketone is recovered from the entrainer by fractionation. The anhydrous acetic acid is recycled to the esterification column. The mixture of diacetate, acetic acid, and sulfuric acid esters from the base of the esterification column is vacuum-distilled and the sulfuric acid esters, left as residue, are recycled as acetylation catalyst. The vacuum distillate is fractionated, the acetic acid is returned to the esterification column, and the glycol diacetate is run to the pyroly-sis unit. The yield of diacetate is 97%, the conversion of glycol to methyl ethyl ketone is 3%, and the acetic acid recovery is quantitative.

The glycol diacetate is pyrolyzed at 595° C. at a contact time of 1.06 seconds. The butadiene is separated from the pyrolysis liquors, washed with water, dried, compressed, and condensed for storage. This butadiene is 99+% pure, and the yield at this point is 83% based on diacetate. The pyrolysis liquors are run to a stripping column where they are contacted with water, and the unsurated acetate components and methyl ethyl ketone are distilled as mixed azeotropes with water. These azeotropes, distilled as mixed azeotropes with water. These azeotropes, which separate on condensation, are run to a decanter from which the water layer returns to the column. The oil layer is fractionally distilled to remove the methyl ethyl ketone and then dried ally distilled to remove the methyl ethyl ketone and then dried by distillation of its water azeotropes to a decanter which returns the water to the original "stripping" column. The dried oils are then distilled to remove impurities boiling above 140° C., and are run to a second small pyrolysis unit. By controlling the water balance in the pyrolysis-liquor stripping column, the base product consists of an acetic acid solution of pyrolysis by-products boiling above 150° C. This solution is run to a still from which the distillate of essentially pure acetic acid is returned to the esterification system. The high-boiling by-products obtained as residue from this operation consist largely of methyl acetyl acetone and a small amount of unpyrolyzed diacetate. This residue is combined with the high-boiling residues from the oils dis-

tillation and run to by-product recovery. The distilled oils from the stripping operation, consisting of a mixture of methyl vinyl carbinol acetate, crotyl acetate, and methyl ethyl ketone enol-acetate (2-acetoxy-2-butene), are pyrolyzed at 595° C. and a contact time of 0.6 second. The butadiene is separated from the pyrolysis liquors, washed with water, dried, compressed, and fractionated to remove high- and low-boiling The purified butadiene is condensed impurities. impurities. The purified butadiene is condensed and combined with the main product from the diacetate pyrolysis. The butadiene obtained in this operation amounts to 5% of the total, and the over-all yield from glycol diacetate is 88% of the theoretical. The pyrolysis liquor from this operation is combined with the liquors from the main pyrolysis and run to the stripping column.

The high-boiling by-products from distillation of the oils and the acetic acid still are steam-stripped to separate methyl acetyl acetone and diacetate from the tars. The water-insoluble portion of the distillate is dried and fractionally distilled, the recovered diacetate returned to the pyrolysis unit, and the methyl acetyl acetone either run to storage or hydrolyzed to methyl ethyl ketone and acetic acid.

Table IV shows the over-all materials balance of the process. in which the materials charged are those required for the production of 100 pounds of butadiene. Under products and recoveries, it is assumed that the methyl acetyl acetone will be hydrolyzed and the methyl ethyl ketone and acetic acid recovered.

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Tank Farm for Storing Butadiene and Styrene at a Synthetic Rubber Plant Operated for the Government by The Firestone Tire & Rubber Company at Lake Charles, La.