Peroxides from Turpentine

Production of Technical Grade Pinane Hydroperoxide

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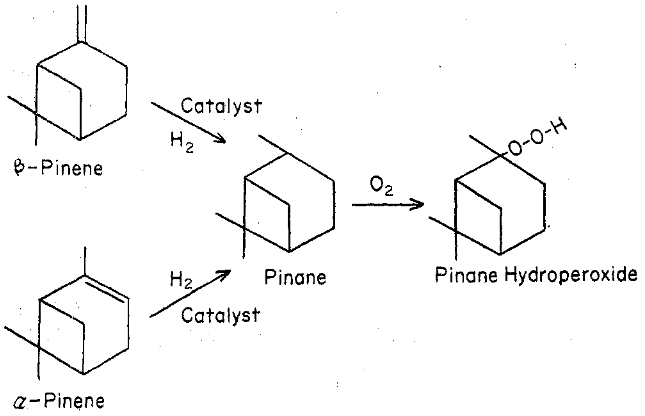
EXCELLENT activity of pinane hydroperoxide as a catalyst for 5° C. GR-S polymerization was reported in the first article in this series (*2*). At that time attention was called to the fact that unusually high conversions and yields of the hydroperoxide can be obtained from pinane. This article discusses in greater detail methods of producing technical grades of pinane hydroperoxide from gum turpentine in good yields. The preparation and properties of pure *cis-l*-pinane-2-hydroperoxide have been described (*3*).



From gum turpentine or pinenes, four steps are involved in producing technical grades of pinane hydroperoxide:

1. Conversion of pinenes to pinane by hydrogenation
2. Purification of the pinane, usually by distillation
3. Oxidation of purified pinane with molecular oxygen to give an oxidate having a peroxide content of about 50%
4. Stripping of the oxidate under vacuum to remove unoxidized pinane and leave the pinane hydroperoxide as the residue.

The product prepared on a 20-mole scale had a purity of 85 to 90%. A conversion of at least 40% per pass and a yield, based on pinane not recovered, of 80 to 90% was obtained.

Peroxide number and degree of unsaturation are tests of product quality

Peroxide Number. The peroxide content of the various oxidates was determined by a slight modification of the iodometric method of Wheeler (*8*). The reaction time was 5 minutes and the results are expressed as peroxide number in milliequivalents per kilogram. The peroxide number of pure pinane hydroperoxide is 11,760.

Unsaturation. The quantitative hydrogenation method of Joshel (*5*) and coworkers was used to determine unsaturation in the various products. The results are calculated in terms of moles of hydrogen absorbed per 136 grams of sample. For convenience, these values are referred to as double bonds per mole in the case of turpentine and are converted to percentage of olefins in the case of crude pinanes.

Sulfuric Acid Test. For rapid control purposes the purity of freshly prepared pinane was estimated by shaking a portion with an equal volume of 85% sulfuric acid for 1 minute and examining the acid layer. Samples that give a cloudy acid layer or a straw color darker than 0.05*N* potassium dichromate solution will generally be unsatisfactory.

Catalytic hydrogenation of pinene to pinane is first step in hydroperoxide production

Pinane is prepared by catalytic hydrogenation of either α- or β-pinene. In the work reported in this article a commercial catalyst containing 16% nickel supported on filter aid and suspended in coconut oil was used. Both high pressure (20 to 100 atm.) and low pressure (15 to 30 pounds per square inch absolute) hydrogenations were made using this catalyst at a 1% nickel level and temperatures in the range of 60° to 150° C.

High Pressure Hydrogenation. In a representative high pressure hydrogenation, 1275 grams of fresh gum turpentine, $n_D^{20} = 1.4715$, $\alpha_D^{26} = 12.60$ (10 cm., neat), $d_4^{20} = 0.8618$, containing an average of 1.03 double bonds per mole were charged to a 3-liter, rocker-type autoclave. Commercial nickel hydrogenation catalyst (70 grams, 14 grams of nickel) was added and the autoclave was closed, flushed with hydrogen, and charged with hydrogen at about 100 atm. The shaker was started and the autoclave was heated electrically to about 60° C. over a period of about 20 minutes by means of an electric furnace. At this point the hydrogenation "caught" and heat was cut off. The hydrogen pressure was permitted to drop to about 20 atm. and then recharged to about 100 atm. The temperature rose to 130° C. during the next 40 minutes and about 0.9 mole of hydrogen was absorbed per mole of turpentine. The heater was then adjusted to maintain this temperature for about 4 hours to complete the hydrogenation. Total hydrogen uptake was about 1

Table I. Effect of Light on Peroxidation of Pinane by Method A

Temp., ° C.	Time, Hours	Oxygen, Ml.		Peroxide Number[a]	
		Light	Dark	Light	Dark
100	6	63[b]	64[b]	2575[b]	2625[b]
80	31	73	72	2900	2875

[a] Peroxide number of pure pinane hydroperoxide is 11,760.
[b] Average of three runs.

Table II. Oxidation of Pinane at 110° C. by Method B

Time, Min.	Peroxide Accumulated, Mole/Mole Pinane Charged	Oxygen Absorbed, Mole/Mole Pinane Charged	Yield, %[a]
35	0.03	0.03	100
92	0.09	0.09	100
184	0.28	0.30	93
255	0.42	0.45	93
300	0.50	0.60	83
368	0.58	0.76	76
410	0.62	0.88	71
447	0.62	0.96	65
533	0.50	1.15	44
630	0.29	1.32	22
682	0.22	1.41	16

[a] (Moles peroxide accumulated/moles oxygen absorbed) × 100.

mole per mole of turpentine. Filtration after the reaction mixture was cooled yielded 1312 grams of crude pinane containing about 30 grams of coconut oil from the catalyst. Distillation of this product through a short Vigreaux column at atmospheric pressure yielded 1020 grams of pinane boiling below 170° C., $n_D^{20} = 1.4615$, $d_4^{20} = 0.8546$, $\alpha_D^{25} = -9.0$ (10 cm., neat), which gave only a light yellow color when it was shaken with 85% sulfuric acid. This represents a yield of about 80% based on the gum turpentine charged.

The recovered catalyst was still fully active and was re-used three times to produce yields of 88, 89, and 87% of pinane. The low yield in the first run was due to the difficulty in removing the last of the pinane from the residual coconut oil.

Low Pressure Hydrogenation. Low pressure hydrogenations were carried out in stirred autoclaves designed for the hydrogenation of fats. The largest single charge was a 400-pound drum of gum turpentine. This hydrogenation was carried out at 22 pounds per square inch gage and 280° F. for 18.5 hours. At this time the run was stopped because of severe leakage at the agitator shaft bearing caused by the action of hot turpentine on the packing. This hydrogenation was only 84% complete—that is, quantitative hydrogenation indicated about 0.17 of a double bond remained per mole of terpene. The original gum turpentine had about 1.05 double bonds per mole, indicating the presence of 5% of monocyclic terpenes, which yield *p*-menthane on hydrogenation. Small scale runs indicated that substantially complete hydrogenation of gum turpentine can be attained at 60 pounds per square inch and 150° C. when a suitable packing is used in the agitator shaft seal.

A portion (2400 grams) of this crude pinane was distilled through an efficient column at about 50:1 reflux ratio to give about 1500 ml. of pinane containing only about 1% of residual olefins.

Small and large scale techniques of pinane oxidation are investigated

Method A. Small samples (2 ml.) of pure pinane (*3*) were oxidized with oxygen in 50-ml. Erlenmeyer flasks attached to gas burets. The reaction temperature was controlled by immersing the reactors in a constant temperature oil bath. The samples were not stirred. The progress of the reaction was followed by observing the volume of oxygen absorbed. At the conclusion of each experiment the peroxide content of the sample was determined.

Method A was used to study the effect of light on the oxidation of pinane. For runs in the dark, the reactors were completely covered with tin foil. A 200-watt incandescent light was used to illuminate the reactors for runs in the light. The results of these experiments are given in Table I.

Method B. Samples of pinane (0.1 mole) were oxidized in 125-ml. Erlenmeyer flasks immersed in a constant temperature oil bath. The samples were stirred by means of a glass-encased magnetic stirring bar, and wet oxygen from a calibrated gas reservoir was passed over the surface of the liquid at the rate of 1 liter per hour. The exit gas was passed through a Dean-Stark trap and condenser to remove entrained vapors, and was then collected in a calibrated gasholder. Samples for use in determining peroxide number were withdrawn by interrupting the oxidation for a few seconds and using the oxygen inlet tube as a pipet to withdraw the sample.

Method B was used to investigate the effect of oxidation temperature on the peroxidation reaction. The results of these experiments are presented in Figure 1 and in Tables II and III. In calculating the data for Tables II and III, allowance was made for the moisture content of the oxygen, for the removal of samples, and for the loss through the condenser by evaporation. Since such calculations involve a number of approximations, the results are only semiquantitative.

Method C. This method was the same as Method B except the reactor was simply connected to an oxygen reservoir and the oxidation was carried out in a closed system. In Table IV results obtained by this method are compared with those obtained by method B.

PINANE HYDROPEROXIDE

. . . is an excellent catalyst for 5° C. GR-S rubber polymerization

. . . can be made from gum turpentine, α-pinene, or β-pinene

. . . yields are good, with purities up to 90%

Method D. Oxidations were made using 100-ml. samples of pinane containing 1.4% of olefins in a 250-ml. reactor with a fritted-glass false bottom for introduction of oxygen and equipped with the usual moisture trap and condenser. A temperature of 110° C. was maintained by means of a constant temperature oil bath, and the oxidation time was 6 hours in each case. The crude oxidates were stripped at 0.3 mm. of mercury pressure to a pot temperature of 78° C. using water vapor as a carrier gas to remove unoxidized pinane. Oxygen absorption was not measured, but peroxide content was determined before and after stripping.

To evaluate the effect of iron on the peroxidation, duplicate runs were made with and without 1 gram of iron filings in the sample and iron turnings in the head space and trap. The runs with iron gave light yellow oxidates having peroxide numbers of 6200 and 6400. Stripping in the presence of iron gave a product having peroxide number of 10,600. The runs without iron gave similar oxidates having peroxide numbers of 5800 and 6600; the stripped product had a peroxide number of 10,800.

Method E. For larger scale runs (10 to 20 moles) using various grades of pinane, the reactor consisted of a 3- or 5-liter, three-necked flask which was fitted with an efficient mechanical stirrer, a fritted-glass gas inlet tube, a thermometer, and a modified Dean-Stark moisture trap and reflux condenser. The reactor was heated with a heating mantle at the start of the oxidation and was cooled with an air blast or with a wet cloth during the latter stages of the reaction. The oxidation was initiated at 120° to 130° C., and the temperature was lowered as the oxidation progressed. Samples were removed from time to time and the peroxide content was determined. Upon completion of the oxidation, the peroxide was concentrated by stripping off the unreacted pinane under vacuum, using water vapor as a carrier gas.

Table III. Oxidation of Pinane at 120° C. by Method B

Time, Min.	Peroxide Accumulated, Mole/Mole Pinane Charged	Oxygen Absorbed, Mole/Mole Pinane Charged	Yield, %[a]
20	0.03	0.03	100
42	0.09	0.09	100
62	0.16	0.16	100
83	0.26	0.27	96
102	0.31	0.40	78
118	0.42	0.53	79
134	0.44	0.65	68
167	0.42	0.84	50
179	0.40	0.88	45
225	0.30	1.06	28
271	0.29	1.19	24
322	0.16	1.33	12

[a] (Mole peroxide accumulated/moles oxygen absorbed) × 100.

Table IV. Oxidation of Pinane by Methods B and C

Temp., ° C.	Max. Peroxide No. Attained by Method		Time to Reach Max. Peroxide No., Hr., by Method	
	B	C	B	C
100	8950	7100	16.3	16.5
110	8300	6000	6.8	5.5
120	6050	2700	2.2	2.0

Oxygen flow rates of 200 to 400 liters per hour were used, depending on the size of the charge. Oxygen absorption was not measured directly, but in some experiments an efficient trap cooled with solid carbon dioxide was used to condense the volatile material from the exit gas. The amount of oxygen absorbed was then estimated from the total weight of products recovered.

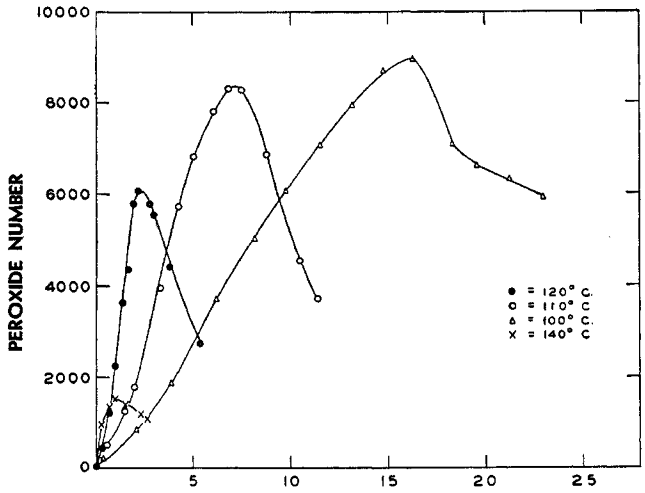


Figure 1. Oxidation of pinane by Method B

Results of experiments using this method are given in Tables V, VI, and VII.

Method F. On the basis of the runs with manual temperature control, the reactor shown in Figure 2 was built for automatic temperature control.

The over-all length of the reactor is about 1 meter. Neck *A* is fitted with a long-stemmed glass thermoregulator. The simple regulator shown in Figure 3 is satisfactory and convenient for this purpose. It is readily set simply by opening the stopcock until the desired temperature is attained and then closing it. Necks *B* and *C* are used for insertion of a thermocouple well (or thermometer) and a sampling tube. Neck *D* is the gas outlet and is fitted with a Dean-Stark moisture trap and reflux condenser.

Table V. Oxidation of Pinanes by Method E

Olefin Content, %	Oxidate		Concentrate		Yield, %[a]
	Peroxide No.	Hours	Peroxide No.	Acid No.	
13	4000	4.5	8100	20	69
4.5	6500	4.8	9600	13	82
1.4	5700	5.5	10,500	5	90

[a] (Moles of hydroperoxide/moles of pinane consumed) × 100.

Table VI. Production of Pinane Hydroperoxide by Method E

	Run Number				
	1	2	3	4	5
Pinane charged, moles	20.9[a]	21.3[b]	21.1[c]	21.6[a]	21.3[d]
Oxygen absorbed[e], moles	8.3	9.5	9.5	10.4	9.45
Peroxide in oxidate, moles	8.7	8.7	8.5	9.8	8.75
Pinane recovered, moles	11.5	11.0	11.5	11.1	11.6
Peroxide in recovered pinane, mole	0.14	0.4	0.4	0.4	0.2
Peroxide in product, moles	7.95	8.2	7.7	9.1	8.0
Pinane consumed[f], moles	9.4	10.3	9.6	10.5	9.7
Conversion, %[g]	41.5	41	40	45.5	41
Yield, %[h]	85	83.5	84.5	90.0	85
Product purity, %[i]	89.6	84.6	85.8	91.7	86

[a] Fresh pinane (0.14% olefins).
[b] Recovered pinane from run 1 plus fresh pinane.
[c] Recovered pinane from run 2 plus fresh pinane.
[d] Recovered pinane from runs 3 and 4.
[e] (Weight of all products − weight of pinane charged)/32.
[f] Includes loss.
[g] (Peroxide in oxidate/pinane charged) × 100.
[h] [(Peroxide in product + peroxide in recovered pinane)/pinane consumed] × 100.
[i] (Peroxide number of product/11,760) × 100.

Table VII. Oxidation of Pinane by Method E with Air and Oxygen

	Oxidate Peroxide No.[a]	Product	
		Grams	Peroxide No.
Air	3700	725	7000
Oxygen	6200	875	9200

[a] After about 5.5 hours oxidation at 110° C.

Table VIII. Oxidation by Method F of Pinane Containing 0.77% Olefins

Time, Min.	Peroxide No.	Temp., ° C.	Oxygen Absorbed, Mole/Mole Pinane Charged	Peroxide Content, Mole/Mole Pinane Charged
0	30	115	0	0.002
10	140	120	0.007	0.009
25	520	130	0.033	0.035
35	..	120	0.077	...
55	..	110	0.100	...
90	1830	109	0.148	0.127
120	2490	111	0.194	0.174
150	3220	109	0.260	0.229
180	3950	112	0.328	0.286
210	4670	109	0.390	0.342
240	5310	110	0.460	0.394
250	5690	109	0.480	0.424
270	6040	110	0.520	0.454
287	6370	110	0.552	0.480
300	6440[a]	50	0.560	0.488

[a] Stripping of this oxidate gave a product of 87% purity; yield of pinane hydroperoxide was 84%.

The coolant may be any suitable high boiling liquid, such as turpentine, and is recirculated through a heat exchanger–reservoir system by means of a centrifugal pump. The flow is controlled by means of a magnetic valve actuated through a relay by the thermoregulator. Heat for initiation of the reaction is provided by wrapping the reactor with electrical heating tape.

Oxygen input and exhaust were measured by means of wet test meters. Samples were withdrawn at suitable intervals for determination of peroxide content. Table VIII presents data for a typical run by this method.

Cold-Rubber Polymerization. Samples of a crude pinane oxidate and a pinane hydroperoxide concentrate were tested by the Government Laboratories of the University of Akron for use in 5° C. copolymerization of butadiene-styrene (*6*). For this evaluation the amine formula II (Formula A) and the low-sugar iron formula (Formula B) previously reported (*1*) and a sugar-free formula (Formula C) were used. The sugar-free formula was identical with the low-sugar formula except for the omission of the sugar and part of the pyrophosphate from the activator. All peroxides were tested simultaneously at a given level. Representative data from these tests are given in Table IX.

Decomposition of Pinane Hydroperoxide. The general technique used in this work consisted of weighing a sample of the pinane hydroperoxide (approximately 0.1 gram) into a small glass ampoule, adding the decomposing agent being tested, flushing the ampoule thoroughly with nitrogen, and sealing it. The sealed ampoules were immersed in a constant temperature bath and removed at suitable intervals, chilled, cleaned thoroughly, and opened. The sample was transferred to a flask by means of the peroxide number solvent and the peroxide content was determined. Decomposition conditions were chosen on the basis of work on the pure peroxide (*3*).

Results of these experiments are given in Tables X, XI, and XII.

Over-all yield of 85% is realized in production of high purity hydroperoxide

Preparation of Pinane. Although gum turpentine was used as the starting material in the work reported, either α- or β-pinene can be used. β-pinene hydrogenates more readily than turpentine or α-pinene and can be hydrogenated at a little lower temperature. When gum turpentine is used instead of pure pinenes, the product may contain up to 5% of *p*-menthane and small amounts of other saturated terpenes, but these do not interfere in the oxidation step.

If the hydrogenation step is carried out properly, the product can be filtered, distilled to remove the last traces of the catalyst and the carrier, and used for the production of pinane hydroperoxide without further purification. If the hydrogenation step is not carried to completion, purification of the crude pinane may be necessary. As shown in Tables V and X, the presence of excessive amounts of residual olefins decreases the purity and stability of the product and the yield of hydroperoxide.

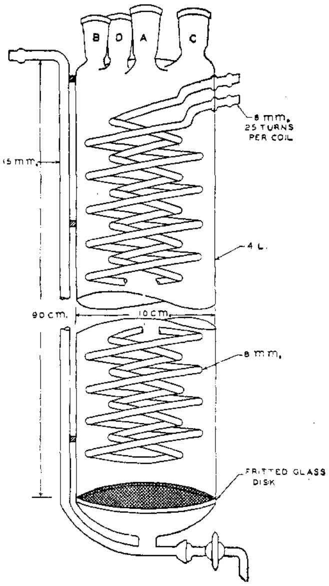


Figure 2. Reactor for oxidation of pinane by Method F

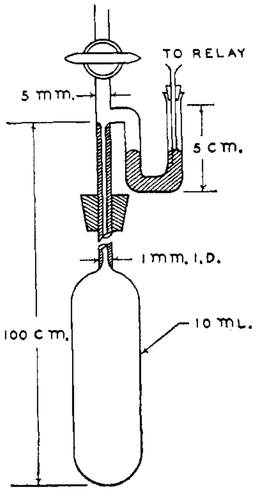


Figure 3. Regulator for automatic temperature control of oxidation of pinane

Table IX. Polymerization of Butadiene-Styrene at 5° C.

A—amine formula
B—low-sugar iron formula
C—sugar-free iron formula

Peroxide		Conversion, %					
		8 Hours			12 Hours		
Purity, %	Part[a]	Formula A	Formula B	Formula C	Formula A	Formula B	Formula C
Pinane Hydroperoxide							
50	0.06	..	51	22	..	56	22
50	0.08	..	56	58	..	78	71
50	0.15	53	..	..	67	..	..
87	0.06	..	71	63	..	81	75
87	0.08	..	67	61[b]	..	83	76[c]
87	0.15	60	..	..	71	..	..
Diisopropylbenzene Monohydroperoxide							
50	0.06	..	55	17	..	57	17
50	0.08	..	73	37	..	85	39[d]
50	0.15	59	..	..	64	..	..

[a] As 100% peroxide, weight basis.
[b] At 0.07-part level conversion was 66%.
[c] At 0.07-part level conversion was 83%.
[d] At 0.09-part level conversion was 63%.

Table X. Decomposition of Technical Grades of Pinane Hydroperoxide for 2 Hours at 110° C.

Peroxide Number		Decomposition, %
Initial	Final[a]	
11,750	10,850	8
10,550[b]	8,900	16
6,000[c]	4,400	27
7,500[d]	4,500	39

[a] Average of two values.
[b] Peroxide concentrate from pinane containing 1.4% olefins.
[c] Oxidate from pinane containing about 10% olefins.
[d] Peroxide concentrate from pinane containing 13% olefins; stored about 6 months before testing.

Table XI. Effect of Additives on Decomposition of Pinane Hydroperoxide at 110° C.

Additive	Additive Concn., %	Time, Hr.	Peroxide No.[a]	Decomposed, %
None	..	1.5	10,840	7.8
None	..	1.5	10,750	8.4
None	..	4	10,300	12.3
Water	5.3	4	10,950	6.9
Nitric acid (concd.)	11.1	4	1,035	87.7
Sulfuric acid (6*N*)	10.9	4	0	100
Acetic acid (glacial)	1.9	4	8,800	25.1
Pinane hydroperoxide by product acids[b]	0.9	4	10,350	11.9
Sodium hydroxide (20%)	4.3	1.5	6,500	44.7
Sodium carbonate	1.7	4	10,300	12.3
Dihexylamine	4.4	1.5	8,850	24.7
Octylamine	2.6	1.5	10,250	12.8
Lead acetate	2.5	1.5	3,160	73.1
Manganese acetate	2.5	4	0	100
Zinc carbonate	1.2	1.5	11,270	4.0
Ferrous sulfate	1.4	1.5	10,500	10.6
Copper foil (old)	1[c]	1.5	Ca50	99.6
Zinc powder	3.2	1.5	10,780	8.2
Iron powder	0.9	4	10,150	13.6
Aluminum powder	1.3	1.5	11,180	5.0

[a] Pinane hydroperoxide = 11,760.
[b] Water-insoluble, nonvolatile acids obtained by extraction of oxidate with alkali, regeneration of acids, extraction, and vacuum drying.
[c] Sq. cm.

Table XII. Effect of Heavy Metal Carbonates on Decomposition of Pinane Hydroperoxide at 100° C.

(Heating time = 1.5 hours)

Carbonate Additive	Additive Concn., %	Peroxide No.	Decomposed, %
None	..	11,550	1.7
Cobalt	1.5	110	99.0
Manganese	2.3	7,260	38.2
Copper	1.4	9,800	16.6
Lead	2.5	11,300	3.8

The residual olefins can be removed by efficient fractional distillation, by washing with concentrated sulfuric acid or with chromic acid–sulfuric acid mixtures, by passage through activated silica gel, or by a combination of these processes. Obviously such methods are relatively time-consuming and expensive. In some cases it has been found satisfactory to oxidize the impure pinane for a short time at 130° to 140° C. and recover the unoxidized pinane by simple distillation. The olefins are more easily oxidized than the pinane. As a general rule it is much better to take adequate precautions to ensure complete hydrogenation than to have to remove residual olefins from the crude pinane. However, the hydrogenation conditions should be fairly mild since high temperatures favor the production of *trans*-pinane (*7*), which is more resistant to oxidation than is *cis*-pinane (*2*). Furthermore, vigorous hydrogenation conditions may convert the pinane to monocyclic hydrocarbons (*4*).

Peroxidation. At the temperatures used in the present investigation, light was found to have no effect on the peroxidation (Table I); hence, no attempt was made to control the illumination in succeeding oxidations.

The rate and maximum extent of peroxide accumulation are both increased by passing an excess of oxygen through the reactor (Table IV). This effect is most pronounced at the higher oxidation temperatures and is probably due both to removal of volatile decomposition catalysts from the system and to maintenance of a high oxygen concentration in the gas phase. The importance of this latter factor is emphasized by the poor results obtained with air as the oxidant (Table VIII). Therefore, a large excess of oxygen was used for the large scale oxidations and the reactors were designed to give efficient contact between the oxygen and the pinane.

As shown in Figure 1 and in Tables I, II, III, and IV, the effect of oxidation temperature is complex. Although the data in Tables II and III are only semiquantitative, they clearly indicate that as the temperature is increased the desired increase in initial rate of peroxide accumulation is counterbalanced by a reduction in the maximum amount of peroxide accumulated (yield). Furthermore, the rate of peroxide accumulation and the conversion of the oxygen absorbed to peroxide decrease before the maximum peroxide content is reached. It appears that the most useful oxidation temperatures lie in the range of 100° to 120° C.

Since good conversion of oxygen to peroxide is obtained in the early stages of the oxidation, even at 120° C., it is practical to start the oxidation at 120° C., or even higher, and subsequently reduce the temperature. Typical runs using this technique to obtain good yields of peroxide rapidly are illustrated in Tables V, VI, VII, and VIII.

Automatic temperature control allows the operator to follow the reaction more closely. Results of a typical run, as shown in Table VIII, are similar to the results obtained with manual control (Table II).

In most of the oxidation it was observed that the peroxide decomposition was accompanied by the accumulation of relatively large amounts of an aqueous layer in the reflux return trap. This aqueous layer from typical large scale oxidations contained 30 to 60% of peroxide, reported as hydrogen peroxide, and was about 2.5N in acidity. About 25 mole % of the acid was acetic acid and the rest was either formic or performic acid.

From the results of Method D, it appears that iron should be a satisfactory material for the construction of reactors and strippers for production of pinane hydroperoxide. There was no evidence of corrosion of the iron. However, these oxidations were terminated before there was any aqueous phase in the trap. In connection with subsequent larger scale preparations it was noted that the aqueous mixture of acid and peroxide which collected in the trap was highly corrosive. Hence, iron would probably not be satisfactory for cold portions of the equipment.

As shown in Table VII, attempts to use air instead of oxygen as the oxidant were unsuccessful. It is not certain whether the failure to obtain satisfactory oxidation rates and conversions was due to a dependence of the rate of peroxidation on the oxygen concentration or was simply due to a failure of the apparatus used to give adequate contact between the air and the pinane. At present it appears that the use of oxygen with proper provisions for recycling it is preferable to the use of air.

Stripping of Oxidates. It was found that the unoxidized pinane could be readily removed from the oxidate by simply evacuating the reactor at the end of the oxidation and passing a carrier gas (air, oxygen, or water vapor) through the oxidate. Pressures of the order of 0.3 to 2.0 mm. of mercury were used in most cases, but pressures as high as 5 to 10 mm. should be satisfactory, especially if a continuous stripper is used. Final pot temperatures as high as 70° to 80° C. resulted in little decomposition of peroxide. Hence, no extensive investigation of stripping conditions was made. In one or two cases, pressures of the order of 0.2 to 0.4 mm. of mercury and pot temperatures of about 90° C. resulted in some distillation of pinane hydroperoxide.

The practicality of recycling recovered pinane is illustrated in Table VI; addition of recovered pinane to a fresh charge did not reduce the yield. From these results it appears that the pinane recovered in the stripping step can be recycled without purification. Hence, about 85% ultimate conversion of pinane to pinane hydroperoxide having a purity of at least 85% may be obtained by this process.

Polymerization. Conversion data from butadiene-styrene copolymerization tests at 5° C. are compared with data obtained simultaneously with diisopropyl-benzene monohydroperoxide in Table IX.

Although these tests were too limited to permit precise evaluation, the results indicate that both the crude oxidate containing about 50% of pinane hydroperoxide and the concentrate are satisfactory indicators for this type of polymerization. Comparison of the results with Formulas B and C suggests that the pinane hydroperoxide may be less sensitive to changes in activator composition than is diisopropylbenzene monohydroperoxide.

Heavy metal salts accelerate decomposition of pinane hydroperoxide

Decomposition. From the data of Tables XI and XII, the following conclusions may be drawn with regard to decomposition catalysts. Water has no effect. Mineral acids are strong decomposition catalysts. Acetic acid causes a definite increase in decomposition rate, but the pinane-derived acids have no effect. Strong aqueous base catalyzes the decomposition but dry sodium carbonate is inert. The organic amines cause decomposition of the peroxide, but it is not clear whether this is due to their basicity or to their reducing action. In the case of the metal salts, both the anion and cation may contribute to the observed effect. For example, the action of the acetates is more pronounced than the carbonates. Among the carbonates tested, the order of activity is cobalt, manganese, copper, lead, and zinc. This is in the same order as their effectiveness as oxidation catalysts and driers. Among the elementary metals, aluminum, iron, and zinc did not accelerate the decomposition, but copper did.

Summary

Technical grades of pinane hydroperoxide having purities of up to 90% can readily be prepared using gum turpentine or its constituents, α-pinene and β-pinene, as the starting material and with pinane as an intermediate. Four steps are involved—hydrogenation of the pinenes to pinane, distillation of the pinane, oxidation, and removal of unoxidized pinane by a stripping distillation. Even without the last step oxidates containing over 50% of pinane hydroperoxide can be obtained. This concentration can be used for many purposes, but the value of the pinane recovered should make the stripping step quite profitable.

Yields in all steps are excellent. The first two steps result in about a 90% yield of satisfactory pinane. Recycling of the less pure cuts will increase this figure. In the oxidation and stripping steps, conditions that permit operation on an 8-hour cycle gave conversions per pass of over 40% and ultimate yields in excess of 85%.

To obtain high quality products rapidly in good yield it is important that the pinane used be substantially free from unsaturated impurities. Temperatures in the range of 120° to 130° C. are helpful in accelerating the oxidation in the initial stages, but the reaction temperature should be lowered to about 105° to 110° C. as the reaction progresses. Light has little effect on the reaction. Iron appears to be harmless but cobalt, copper, and similar heavy metals and their salts must be rigorously excluded. It is essential to maintain vigorous agitation and a strong flow of oxygen during the oxidation step. Failure to provide adequate contact between the oxygen and the pinane slows the rate of oxidation and lowers the yield per pass that can be obtained without excessive production of by-products.

Pinane hydroperoxide is relatively stable. Oxygenated by-products, particularly those from unsaturated impurities, reduce the stability.

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gineering and development section of the Southern Utilization Research Branch for hydrogenating 50 gallons of gum turpentine.

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Conservation of Butylenes in Butadiene Manufacture

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DEVELOPMENT of a suitable catalyst has resulted in the commercial dehydrogenation of *n*-butenes to 1,3-butadiene. This article describes the history, production and performance, operating problems, testing methods, and economic factors involved in the development and use of a calcium-nickel phosphate catalyst, designated as Type B catalyst. Some of the data have come from the operation of butadiene plants, and some were made available through the Reconstruction Finance Corp.

Past difficulties have been minimized in this presentation. Though serious at the time, they have shown the way to successful operation. There are few operating troubles that have not been solved.

History of catalyst development includes pilot plant and trial production runs

The Dow Chemical Co. was interested in synthetic rubber well before the start of World War II. The main interest was in styrene; however, considerable thought was given to the problems of making synthetic rubber. In April 1941, E. C. Britton, the 1952 President of the American Chemical Society, and A. J. Dietzler of the Organic Research Laboratory of the Dow Chemical Co. invented on paper a selective catalyst for the dehydrogenation of *n*-butene to 1,3-butadiene. A small amount of the catalyst was made by coprecipitating calcium, nickel, and phosphate radicals in an aqueous medium. The material performed satisfactorily when it was catalytically tested.

Two years later the details were worked out for the preparation of the present Type B catalyst. This is the original calcium-nickel phosphate promoted with chromic oxide to make the catalyst function better and last longer. Preparation methods were described in the only other article previously published on this subject (*1*). The article also contained sections concerning definition of terms and scope of the catalyst that may aid in the understanding of the present article. The first five United States patents on the catalyst were also listed. There has been one more recent patent (*7*), which discusses the materials of construction to be used inside of a commercial Type B catalyst reactor.

In April 1945, the chemical engineering laboratory of Dow started to develop the commercial process for preparing Type B catalyst for butadiene pilot plant work and sale to butadiene producers. Type B catalyst is sold as pellets, $^3/_{16}$ inch in diameter and $^3/_{16}$ inch long, packed in 400-pound-net-weight steel drums. The selling price has been in the vicinity of $1.50 per pound. The pellets as received are not ready for use until the 2% by weight of graphite pelletizing agent is removed by roasting the catalyst in the presence of steam and air.

Pilot plant work was carried out in 1945 using a small ethylbenzene dehydrogenation furnace located at Sarnia, Canada. Full scale operation was first observed in 1946, also at Sarnia, but was not successful. Two more trial runs were made in 1950, at Sarnia, with fair success. These operations have been described in detail by Reilly (*9*).

Reilly (*9*) also revealed that Polymer Corp., Ltd., first used this catalyst for successful commercial operation on July 24, 1951. Six-foot beds were used in two of the four Jersey-type design adiabatic reactors. Success in the other two reactors was achieved on September 11, 1951. Since then, all of Polymer Corp.'s butadiene has been made over Type B catalyst. At Baytown, Tex., the Humble Oil and Refining Co.-operated RFC plant has been 50% commercially on Type B catalyst since June 25, 1952. These facilities are similar to those of the Polymer Corp. Humble made one early experimental run using a 3-foot bed of catalyst; later commercial runs have used 6-foot beds. At Borger, Tex., the Phillips Chemical Co.-operated RFC plant has been experimenting since August 16, 1951, with Type B catalyst on a relatively smaller scale, in one of their four isothermal butadiene production units.

Production and performance evaluations are made from commercial production of butadiene

The three operators have produced (as of May 18, 1953) approximately 93,000 short tons of butadiene using Type B catalyst. This production figure is based on the following starting dates—Polymer Corp., July 24, 1951; Humble, June 25, 1952; and Phillips, August 16, 1951. Catalyst consumption has been 500 tons, of which an estimated 185 tons was still in use, with an average of 42% useful life remaining, in May of 1953. Assumptions were 1 week turn around time between runs, 7 months of catalyst life, and 95% recovery of butadiene made in the reactor.

About 220 tons of butadiene was recovered each day using the 185 tons of catalyst. This 220 tons is equivalent to 15% of the rated capacity of all petroleum butadiene plants of the RFC (*2*). (Most of the petroleum butadiene is made in Canada.)

The 220-ton production has been made by ten different runs; six have been completed for an average of 7.0 months of actual on-stream usage. Of the ten, the six runs reflecting the best operating techniques were on stream an average of 99.2% of the time, as of May 18, 1953, not including the time between runs. Of the four runs remaining, two were current runs for which the data were not known. The other two were completed runs that had long periods of down time due to fires or mechanical failures that were not directly connected with catalyst operational problems.