GUM FORMATION IN CRACKED GASOLINES

POLYMERIZATION OF CYCLOPENTADIENE

By

L. Ackermann

Department of Chemical Technology, Technical University, Budapest

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Presented by I. Szebényi

As known, in untreated cracked gasoline distillates, particularly if these are products of thermal cracking, some compounds of higher molecular weight are formed during storage as a result of undesirable processes. When the gasoline is evaporated, these compounds are left back in the form of a so-called gum. This gum formation may become quite substantial if the gasoline comes into contact with metals or air. Light also enhances the gum formation.

During storage for longer time, deposits may be formed also from straight-run gasolines on the walls below the liquid level and discolouration may occur if the glass vessel used for storage is exposed to light. Most probably this phenomenon is a result of the oxidation of substituted naphthenes present in the gasoline [1].

Two kinds of gum content can be distinguished. The quantity of gum detectable in the fuel at the time of testing is designated as the "existent gum" [2]. Besides this the American standard specifications [3] distinguish between gum proper and high-boiling residues; the latter can be extracted with heptane.

The quantity of gum designated as "potential gum" or "gum after oxidation", is that which is detectable in the gasoline after being exposed to an oxygen pressure of 7 kp per cm^2, at 100 °C, for 4 hours [4].

Data on the induction period give information about the tendency of the gasoline to yield gum during storage. The method of determination is in principle the same according to either the Hungarian [5] or the U.S. [6] standard specifications. According to the definition given in the Hungarian standard "the induction period of gasolines is the time in minutes during which the sample of the gasoline is practically not oxidized under prescribed conditions, at 100 °C, exposed to an oxygen pressure of 7 kp per cm^2". The end of the induction period is indicated by a decrease of pressure.

The presence of compounds that tend to form gums is undesirable since while gasoline evaporates, compounds of higher boiling points form deposits in the fuel intake system of the internal combustion engines. Simultaneously with gum formation also the octane rating of the fuel deteriorates, most probably in consequence of the formation of peroxides which enhance knocking.

In order to elucidate the mechanism of gum formation, researchers studied the structure of gums separated from motor fuels variously treated as well as that of products obtained from several model substances. Since some facts pointed to auto-oxidation as playing an important role in the process of gum formation, all studies started in this direction and differed mainly by the choice of the conditions of oxidation. By up-to-date testing methods, the following types of compounds have been detected in the gums: alkylbenzenes, indanes, indenes, styrenes, naphthalenes, dihydronaphthalenes, acenaphthenes, olefins, diolefins, paraffins and cyclo-paraffins.

In their study on the effect of peroxides in cracked gasolines, **Morrel** et al. [7] have found that emergence of peroxides is the first indication of deterioration during storage. Increase of the concentration of peroxides goes hand in hand with colouration, increased gum formation, and loss of antiknock value. Gum formation is an autocatalytic process accelerated by the peroxides formed in the initial stage. They have stated that induction periods are considerably shortened by the addition of peroxide. The same effect results when natural inhibitors are removed [8]. On the other hand, if cracked gasoline is evaporated in an atmosphere free of oxygen, the gummy residue will be less when peroxides initially present had been removed.

In their study of peroxides, aldehydes, acids, and resins formed during storage of cracked gasolines, **Dryer** et al. [9] have found that peroxides are already present when aldehydes, acids and gum have not yet been formed in appreciable quantities. Significant quantities of gum are formed when peroxides are present in substantial amounts, though the quantities of aldehydes and acids are not yet significant.

According to **Rosewald** [10], in the first stage of peroxide formation an "active" hydrocarbon reacts with oxygen. In the case of olefins this reaction might proceed as follows:

$$1.\ \mathrm{C}_x\mathrm{H}_y + \mathrm{O}_2 \rightarrow \mathrm{C}_x\mathrm{H}_{y-1}\mathrm{O} - \mathrm{OH}$$

$$2.\ n(\mathrm{C}_x\mathrm{H}_y) + n\mathrm{O}_2 \rightarrow (-\mathrm{C}_x\mathrm{H}_y\mathrm{O} - \mathrm{O} -)_n$$

Hydroperoxide is formed by substitution, in the first reaction; a di-substituted peroxide by addition, in the second.

The scheme of hydroperoxide formation is

a) $\mathrm{RH} \rightarrow \mathrm{R}\cdot$

b) $\mathrm{R}\cdot + \mathrm{O}_2 \rightarrow \mathrm{R{-}O{-}O}\cdot$

c) $\mathrm{R{-}O{-}O}\cdot + \mathrm{RH} \rightarrow \mathrm{R{-}O{-}OH} + \mathrm{R}\cdot$

d) $\mathrm{R}\cdot + \mathrm{R}\cdot \rightarrow \mathrm{R{-}R}$

e) $\mathrm{R{-}O{-}O}\cdot + \mathrm{R}\cdot \rightarrow \mathrm{R{-}O{-}O{-}R}$

f) $\mathrm{R{-}O{-}O}\cdot + \mathrm{R{-}O{-}O}\cdot \rightarrow\ ?$

In step *a)* a free radical was formed from the hydrocarbon, this is the initiation reaction. In the propagation reactions *b)* and *c)* the free radical reacts with oxygen to yield a free peroxide radical which, in turn, reacts with a further hydrocarbon molecule whereby a further free radical is produced besides a hydroperoxide. Repetition of these two steps carries on oxidation till the chain is terminated with one of the reactions *d)*, *e)*, or *f)*.

Studies of KAWAHARA [11] have shown that, besides oxygen, sulphur compounds also play an important part in the formation of gums. Elemental analysis of the gums studied by him proved that sulphur accumulated in the gum up to a concentration six times the original value. It was also stated that most of the sulphur present is in the form of thio-ethers.

Metal ions initiate the formation of alkoxy-radicals which helps gum formation by converting hydroperoxides into alkoxy radicals

$$\mathrm{ROOH} + \mathrm{Fe}^{++} \rightarrow \mathrm{Fe}^{+++} + \mathrm{OH}^{-} + \mathrm{RO}\cdot$$

That metal ions are responsible for an increased gum formation has been observed already by STORY et al. [12] when they determined gums in glass vessels but had added small quantities of copper oxide to the gasoline. The effect of copper oxide was evident by an, once tenfold, increase of the gum formed.

PEDERSEN [13] made a detailed study of the effects of copper and other metals on the formation of gums, determining in what degree the induction period was shortened, e. g. by various copper compounds.

The catalytic effect of copper can be explained on hand of the following scheme:

I. Cu + peroxide $\rightarrow \mathrm{Cu}^{++}$ + chain initiating free radical
   Cu^{+} + peroxide $\rightarrow \mathrm{Cu}^{++}$ + chain initiating free radical
II. Cu^{++} + reducing agent $\rightarrow \mathrm{Cu}^{+}$
   Cu^{++} + antioxidant $\rightarrow \mathrm{Cu}^{+}$ + $(\text{antioxidant} - \text{one electron})^{+}$

The reactions of copper metal with peroxides, and those of divalent copper ions with antioxidants, are very rapid. On the other hand, reactions of antioxidants with peroxides, at room temperatures, are rather slow but become very rapid if traces of copper are present.

The effects of other metals besides copper have been studied and a series in order of decreasing activity has been established as follows: copper, cobalt, manganese, iron, nickel, chromium, in quantities equivalent with copper.

The stability of cracked gasolines during storage can be increased with inhibitors and metal-desactivators. The inhibitors are compounds, mainly substituted phenols, of which very small amounts, say one hundredth, even one thousandth per cent, suffice to delay gum formation significantly, or to protract its induction period. These compounds are effective in so far as they terminate the chain reaction initiated by the peroxide formed in the oxidation process, i.e. according to the equation

$$ROO^{\cdot} + AH \rightarrow RO{-}OH + A^{\cdot}$$

where

$ROO^{\cdot}$ is a chain propagating peroxide radical
AH is an inhibitor of the phenol type
ROOH is a hydroperoxide
$A^{\cdot}$ is an inactive radical produced from the inhibitor.

The antioxidant effect is the function of the original induction period of the gasoline, as well as of its original stability. Generally, the use of an inhibitor discolours the gasoline. With some inhibitors this effect is so strong that they cannot be used in practice though their inhibiting effect is good.

Much research has been done in the field of inhibitors. ROSENWALD and HOATSON [14] studied the correlation between the quantity of inhibitors tested and their inhibiting effect. EGLOFF [15], testing several types of compounds, studied the influence of the nature and position of substituent groups on the inhibiting effect. NIXON et al. [16] tested the inhibiting effect of 36 mono-, di-, and tri-substituted phenols, comparing their efficiency with that of 2,6-di-tertiary-butyl-4-methyl-phenol, chosen as the reference substance.

There are three methods to eliminate the detrimental effect of copper, *viz.*

a) prevention of the entrance of copper ions into the gasoline
b) the removal of copper ions
c) desactivation of copper ions.

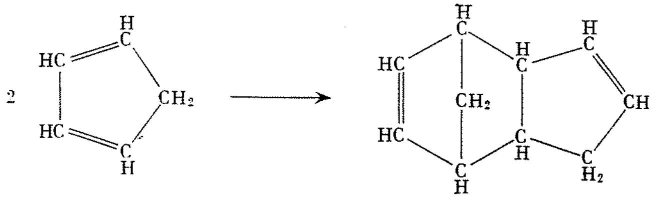
In practice the last method is the best, because it works even when copper ions get into the gasoline later, whereas the removal of copper ions does not protect the gasolines against subsequent contamination. The active substance of one of the best known copper deactivators is N,N'-disalicylidene-1,2-diamino-propane; this forms a chelate with divalent copper ions.

Experimental

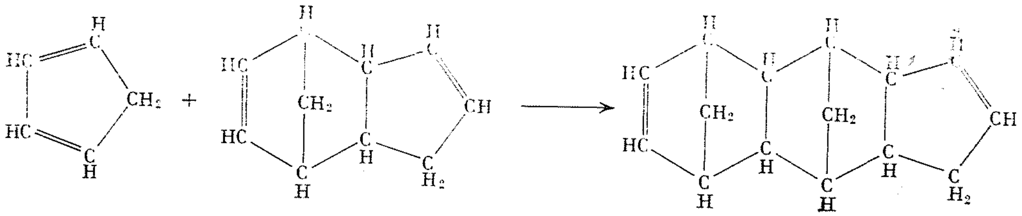
The aim of this work was to find out how far the polymerization of the diene chosen as a model compound is affected by the following factors: 1. temperature, 2. light, 3. oxygen atmosphere, 4. concentration.

Cyclopentadiene was used as model compound because *a)* it is one of the representatives of the compounds liable to polymerize in gasolines produced by thermal cracking; *b)* the pure monomer is easily prepared, thus always a well defined, uniform substance can be used for each run; *c)* the polymerization of cyclopentadiene is a process rapid enough to allow tests to be carried out within a short time and give results that can be evaluated correctly, but not as rapid as to prevent keeping track of how it proceeds; *d)* the analysis of both the starting material and products can be performed without difficulty and with a sufficient accuracy by gas chromatography.

On the basis of studies concerning structures, **Alder** and **Stein** [17] have shown that in dicyclopentadiene the two cyclopentadiene molecules are linked in the following manner



The addition of further cyclopentadiene molecules occurs according to the following scheme



According to data in the literature [18], only five, according to other findings [17], seven molecules can unite in this way, even at elevated temperatures. At room temperature only dicyclopentadiene is formed.

The samples to be tested were stored under the following conditions.

1. To test the effect of temperature, parallel samples kept in perfectly closed brown glass bottles of 20 ml capacity were stored in darkness *a)* at room temperature, *b)* at —20 °C. Air was enclosed above the liquid phase in each bottle.

2. Samples, prepared as before, were irradiated in quartz test tubes, with a 300 W quartz lamp from a distance of 70 cm, for 36 hours. Here too, air was enclosed above the liquid phase.

3. To test the effect of oxygen atmosphere, the samples were filled into Erlenmeyer flasks of 25 ml capacity each, and these were placed in a pressure vessel kept at 4 kp per cm^2 oxygen pressure. By suitable closure, contact of oxygen with the samples was assured without allowing errors due to losses by evaporation to exceed an inevitable minimum.

4. To test the effects of concentration, besides pure cyclopentadiene, diluted samples were also tested. Such samples were prepared by dilution of the freshly monomerized cyclopentadiene, in ratios of 1 : 1, 1 : 2, 1 : 5, and 1 : 10 by weight with n-hexane and benzene, respectively. The aim of using two different types of solvents was to see whether the nature of the diluent

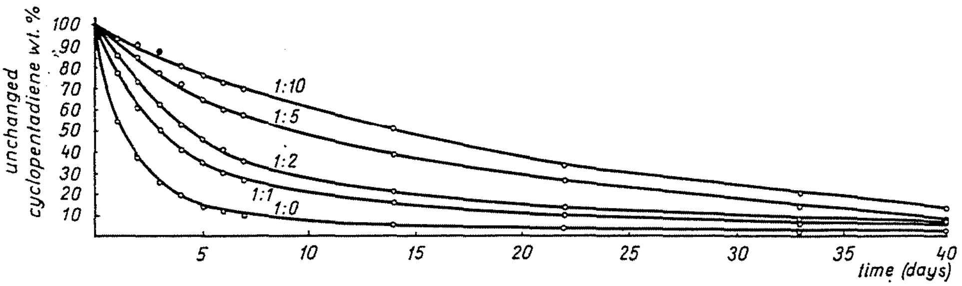


Fig. 1. Change of cyclopentadiene content of samples stored in darkness at room temperature Diluent: n-hexane

(paraffinic or aromatic hydrocarbon) had any effect upon the degree and rate of polymerization.

It was not the purpose of this work to establish the ratio of dicyclopentadiene to eventual higher polymers in the products obtained, but only to determine the time-dependent quantity of cyclopentadiene converted under various conditions. The obvious, or better the only method for this seemed to be to determine the amount of monomer still present at suitable intervals.

The tests were carried out with a gas chromatograph AEROGRAPH Model 90-P3, in conjunction with a recorder VARIAN Model G-14A-1. Commercial columns, made of metal spiral tubes of 1.5 m length, 6 mm o.d., with their original packings, were used. The packing used for testing a part of the samples diluted with n-hexane was 10 per cent of β,β'-oxydipropionitrile, on 60 to 80 mesh fire-brick grains, while for the rest of the samples a column packed with 20 per cent of a SE-30 silicon-polymer on 60 to 80 mesh Chromosorb W was used.

Since no integrator was available, and the measurement of the areas under more than 2000 peaks* by planimetry would have been too tedious and difficult, suitable calibration curves were prepared prior to the determinations and the quantity of unconverted cyclopentadiene was determined on the basis of the ratios of peak heights. The reference peak was that of the pure diluent. In the case of undiluted cyclopentadiene the measurements were carried out by adding known amounts of n-hexane, or benzene, to an aliquot part of the samples.

Figs 1 to 8 show the quantities of unchanged cyclopentadiene as a function of time.

In the course of testing, the following could be noted.

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* The determination of 366 data, based on measurements of two peaks in 3 or 4 parallel tests.

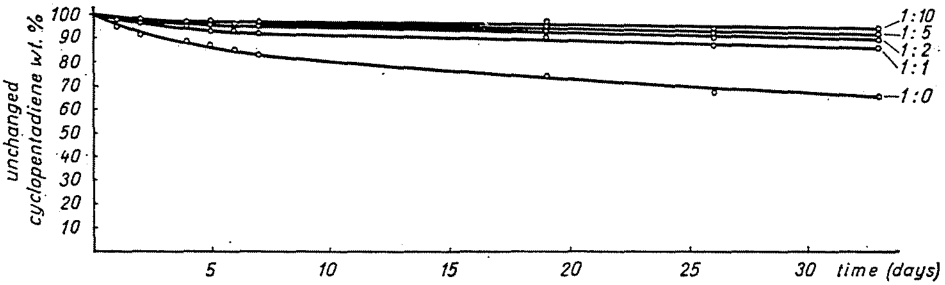

Fig. 2. Change of cyclopentadiene content of samples stored in darkness at —20 °C. Diluent: n-hexane

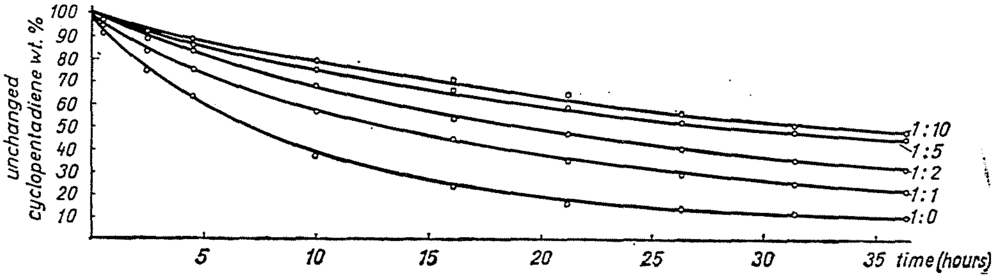

Fig. 3. Change of cyclopentadiene content of samples exposed to ultra-violet light. Diluent: n-hexane

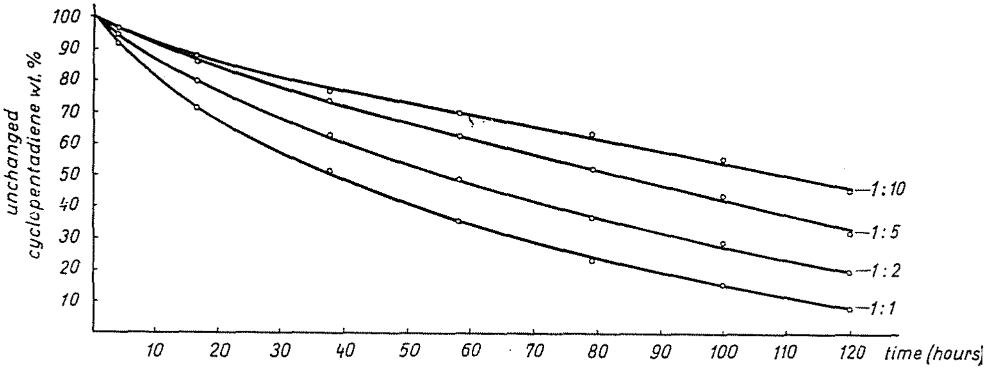

Fig. 4. Change of cyclopentadiene content of samples exposed to an oxygen pressure of 4 kp per cm^2. Diluent: n-hexane

On the walls of the bottles containing the samples diluted with n-hexane and stored in darkness at room temperature, a thin layer of dicyclopentadiene was deposited owing to its poor solubility in this solvent.

Irradiation with ultra-violet light caused turbidity within a short time in samples diluted with n-hexane, because poorly soluble dicyclopentadiene

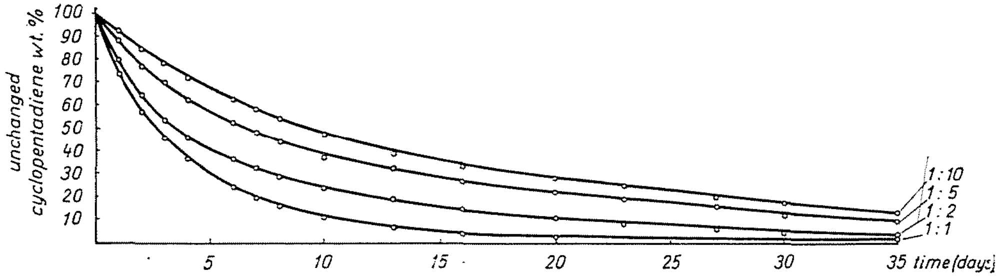

Fig. 5. Change of cyclopentadiene content of samples stored in darkness at room temperature. Diluent: benzene

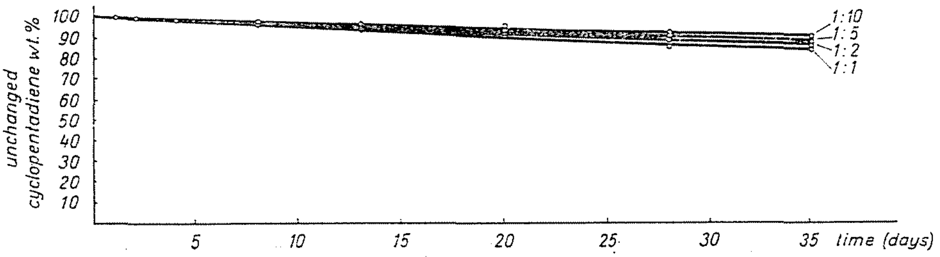

Fig. 6. Change of cyclopentadiene content of samples stored in darkness at —20 °C. Diluent: benzene

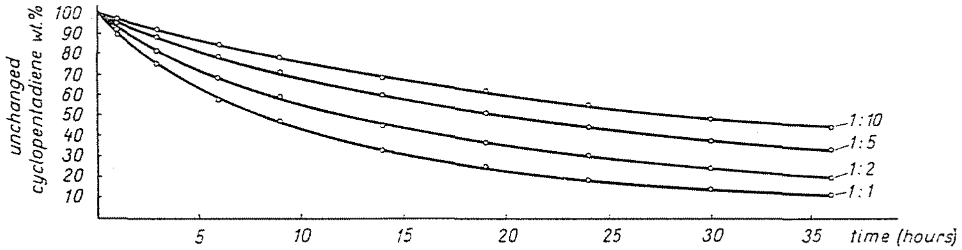

Fig. 7. Change of cyclopentadiene content in samples exposed to ultra-violet light. Diluent: benzene

had formed. Later on these samples turned yellow, still later a light yellow, then brown, resinous deposit separated from them on the quartz tubes in a discontinuous layer. This deposit was insoluble in organic solvents and could not be removed but with chromic-sulphuric acid. A similar phenomenon could be noted in the case of samples kept under 4 kp/cm^2 oxygen pressure.

No deposit was formed in samples diluted with benzene, but according to its concentration, the dicyclopentadiene dissolved raised the viscosity of the samples in various degrees.

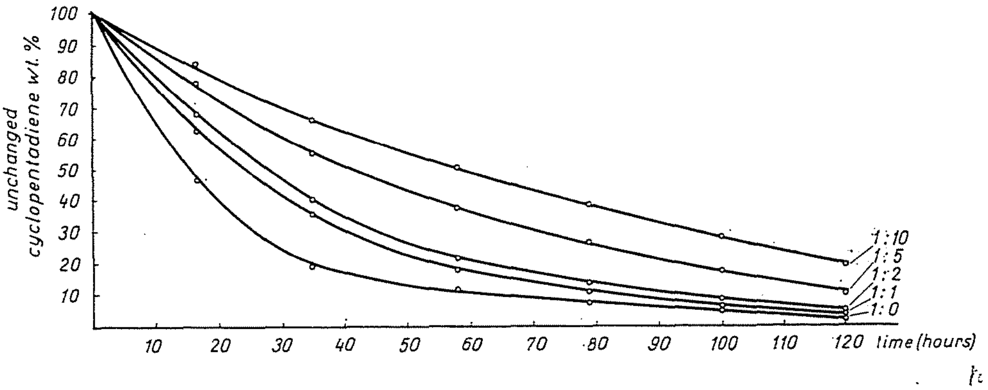

Fig. 8. Change of cyclopentadiene content of samples exposed to an oxygen pressure of 4 kp per cm^2. Diluent: benzene

Samples diluted to 1 : 5, and 1 : 10 ratios by weight and kept at —20 °C, congealed.

With samples diluted with benzene in the ratio of 1 : 1 and irradiated with ultra-violet light, also inhibition tests were carried out. p-Phenylenediamine inhibitor was added in concentrations of 0.02, and 0.002 per cent. Since results of tests carried out in this way coincided with results of tests without inhibitor, other conditions being the same, it was established that under the experimental conditions of the tests, p-phenylenediamine is ineffective though otherwise it is an effective inhibitor. During the experiments the samples became more or less coloured depending on the concentration of p-phenylenediamine added; this seems to point to the oxidation of this compound.

That the inhibitor proved ineffective may be explained in two ways.

a) Polymerization proceeds without the formation of peroxides, according to the equations mentioned before. Thus, in fact, the inhibitor cannot act. The oxidation of p-phenylenediamine must be ascribed in this case to the oxygen in the atmosphere above the liquid.

b) The polymerization goes *via* the peroxides but at such a high rate that the relatively small amount of the inhibitor is oxidized very rapidly and thus a lengthening of the induction period cannot be detected.

The first hypothesis seems to be supported by the fact that in the liquid phase a substantial amount of dicyclopentadiene was present. On the other hand, the fact that on the walls of the quartz test tubes solid drops of gum insoluble in organic solvents could form, shows that cyclopentadiene irradiated with ultra-violet light polymerized into higher polymers. The formation of a similar resinous product was experienced in tests carried out under oxygen pressure. Also according to reference [18], cyclopentadiene yields peroxides under oxygen pressure, that explains the formation of the hard resin at a high degree of polymerization.

That this hard resin formed equally in samples exposed to ultra-violet light and in those exposed to oxygen pressure, further the substantial quantity of dicyclopentadiene detected in the liquid phase, suggested that polymerization proceeded according to the same mechanism in both cases, *viz.* partially by the direct route and partially *via* peroxides, thus also ultra-violet irradiation would produce peroxides in the presence of oxygen.

From a comparison of results gathered in different series of tests the following conclusions can be drawn.

1. At room temperature, protected from light, undiluted cyclopentadiene is converted practically completely into dicyclopentadiene within 35 days. This result is in good agreement with data published in the literature.

2. The rate of dimerization is decreased by dilution. The shapes of the individual curves representing the decrease of cyclopentadiene content in the samples diluted in different ratios suggest that conversion will go to completion in every case. The time needed for complete conversion is a function of concentration and of circumstances of storage.

3. An aromatic diluent (benzene) delays polymerization less than does a paraffinic one (n-hexane). Thus, for instance, at room temperature during the same time, dimerization in a sample diluted in a 1 : 10 ratio by weight with benzene is the same as in a sample diluted in a 1 : 5 ratio by weight with n-hexane.

4. The difference in the polymerization retarding effect of the two diluents vanishes with increased dilution in the case of samples exposed to ultra-violet light. While data for a sample diluted to 1 : 1 with n-hexane are the same as data for a sample diluted to 1 : 2 with benzene, at a 1 : 10 dilution with any of the two diluents the results differ but slightly. In the case of other treatments a similar phenomenon could not be observed.

5. Ultra-violet irradiation for 36 hours of samples diluted with benzene causes the same degree of polymerization as does standing in darkness for 10 days.

In samples diluted with n-hexane, this correlation is not as clear as that, for, according to concentrations, standing in darkness at room temperature for 9 to 13 days corresponds to ultra-violet irradiation for 36 hours.

6. Under the test conditions the rate of polymerization of undiluted cyclopentadiene exposed to ultra-violet light was twice that of a similar sample kept under an oxygen pressure of 4 kp per cm^2.

7. Under an oxygen pressure of 4 kp per cm^2 the polymerization of a sample diluted to 1 : 1 with benzene is one and a half time as fast, in samples diluted to 1 : 2, 1 : 5, and 1 : 10, about twice as fast as in samples diluted with n-hexane in the same ratios.

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Summary

Series of tests were performed in order to establish how temperature, light, oxygen pressure, and dilution affect the polymerization of cyclopentadiene. n-Hexane and benzene were used as diluents; 1 : 1, 1 : 2, 1 : 5, and 1 : 10 being the ratios by weight of dilutions for both solvents.

The progress of polymerization was tested by determining monomer contents at intervals by means of gas chromatography, using the method of the ratios of peak heights.

Based on the experimental results, it can be stated that a decrease of the concentration of cyclopentadiene (dilution) retards polymerization, and that this retardation is less when an aromatic solvent (benzene) instead of a paraffinic solvent (n-hexane) is used as the diluent.

Low temperature (—20 °C) much retards, but does not prevent, polymerization. When ultra-violet irradiation and oxygen pressure are applied, polymerization proceeds in part *via* peroxides and also some hard gum is formed, though the bulk of the cyclopentadiene is converted into dicyclopentadiene even in these cases. Most probably, after a longer period, a larger quantity would be converted into gum.

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László Ackermann, Budapest XI., Budafoki út 8, Hungary