thiocyanate in 25 cc. of water. The combined solution was slowly evaporated until a friable solid mass was obtained. This was allowed to stand overnight, then pulverized and washed with boiling water. It was then repeatedly washed with hot water, made strongly ammoniacal and alkaline by the use of sodium and ammonium hydroxide solutions. The compound was finally washed with ethanol and with ether. Some was recrystallized from benzyl alcohol but was not improved by this treatment: yield, about 4 g.; platelets of faint yellow color, m. p. 198–199°; persistent bitter taste.

Summary

Derivatives of dulcin have been prepared in which the N side chain is altered and in which the phenetyl group is duplicated; these are tasteless. Substitution of the ether oxygen of dulcin by sulfur gives tasteless derivatives, while substitution of both oxygens by sulfur yields compounds with a very bitter taste. Seven new compounds are reported.

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NATURAL AND SYNTHETIC RUBBER. VI. THE PYROLYSIS OF NATURAL RUBBER IN THE PRESENCE OF METALLIC OXIDES

BY THOMAS MIDGLEY, JR., AND ALBERT L. HENNE

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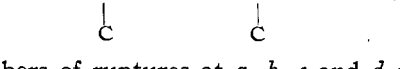
The first paper of this series[1] describes the influence of metals on the pyrolysis of natural rubber: it shows that the presence of a metal does not change the nature of the pyrolysis products, but affects their relative proportions. In this respect magnesium and zinc are most active. The fact that both zinc oxide and magnesium oxide influence the vulcanization process makes it desirable to study the influence of these compounds on the pyrolysis of rubber.

Experiments similar to these previously reported show that zinc oxide or magnesium oxide acts similarly to zinc or magnesium; zinc oxide has by far the stronger effect. Briefly the nature and proportion of pyrolysis products obtained with zinc oxide duplicate those obtained with magnesium, within experimental error.

Let the rubber molecule be represented by a long open-chain formula, and the various bonds of the chain be designated by letters



The relative numbers of ruptures at *a*, *b*, *c* and *d* during the pyrolysis of straight rubber have been computed from the data previously reported, and are represented by $a = 0$, $b = 0.6$, $c = 100$ and $d = 0.7$. However, a similar computation indicates that, in the case of rubber pyrolyzed with

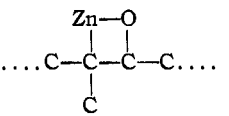
[1] Midgley and Henne. THIS JOURNAL, **51**, 1215 (1929).

magnesium, the ruptures are as follows: $a = 0$, $b = 12.7$, $c = 100$ and $d = 12.1$. In both cases b equals d within experimental error.

Since zinc oxide has the same effect as magnesium upon pyrolysis, it appears that its presence multiplies by about 17 the number of ruptures of the b and d-bonds.

If d and b derive their strength from the fact that they are adjacent to the double bond a, it may be expected that any agent affecting the unsaturation of a will increase the similarity of d and b to c. If the agent be such as to remove entirely the unsaturated character of a, the bonds d, b and c might even become almost identical in strength, though complete identity would be prevented by the presence of the methyl side chains.

However, the formation of a chemical individual such as



with a zinc oxide molecule linked on the carbon chain by chemical valences does not seem to be supported by the facts: the pyrolysis products do not contain any compound formed by rupture of the chain at a; no oxygenated product is to be detected; and zinc oxide is not in the least reduced to the metal. Moreover, the seventh paper of this series shows that ruptures of a do occur in the pyrolysis of hard rubber where a is chemically saturated with sulfur.

Summary

Pale crepe rubber pyrolyzed in the presence of zinc oxide or magnesium oxide gives the same decomposition products as in the absence of the oxides, but in different proportions. This modification is attributed to an action of the oxides upon the double bonds of the rubber molecule.

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