1

2,892,877

PROCESS FOR THE CONVERSION OF PARAFFIN INTO RUBBER-LIKE PRODUCTS

Helmut Kolling, Duisburg-Hamborn, and Heinz Noeske and Friedrich Rappen, Oberhausen-Sterkrade, Germany, assignors to Ruhrchemie Aktiengeselischaft, Oberhausen-Holten, Germany, a corporation of Germany

No Drawing. Application July 29, 1955 Serial No. 525,376

Claims priority, application Germany August 5, 1954 6 Claims. (Cl. 260—677)

This invention relates to conversion of paraffins into rubber-like products.

It is known that paraffin, which is solid at normal temperature, may be converted into hydrocarbons containing olefinic bonds by chlorination and subsequent dehydrochlorination. In this known product less than 1 gram atom of chlorine is generally added per mol of hydrocarbon in order to obtain as high as possible a yield of mono-olefinic products.

It has also been suggested to convert hard paraffin from the Fischer-Tropsch synthesis or fractions obtained from hard paraffin into flexible waxes having properties which correspond to microcrystalline petroleum waxes. This conversion is effected by the addition of more than 1 gram atom, as, for example, 2–4 gram atoms of chlorine per mole of hydrocarbon to the hard paraffin or fraction, and by thereafter subjecting the chlorinated products to a dehydrochlorination.

In accordance with the invention it has now been discovered that paraffin having more than 20 carbon atoms in the molecule may be readily converted into rubber (caoutchouc)-like products by adding more than 4 gram atoms of chlorine, and preferably 6-10 gram atoms of chlorine per mole of paraffin, and subsequently subjecting the reaction products obtained to a dehydrochlorination.

The quantity of chlorine to be added is dependent upon the average number of carbon atoms in the initial paraffin. About 6 gram atoms of chlorine per mole should be added to hard paraffin from the Fischer-Tropsch synthesis, having, for example, a boiling range of above about 460° C. and an average number of carbon atoms of about 45. Paraffins having a lower number of carbon 50 atoms such as slab paraffins require 7–8 gram atoms of chlorine per mole, while about 10 gram atoms of chlorine per mole must be added to paraffin having a still lower number of carbon atoms, such as soft paraffins.

The chlorination in accordance with the invention is effected in the conventional manner by introducing gaseous chlorine into the melted hard paraffin at a temperature ranging slightly above the melting point of the paraffin. The chlorination may be effected at normal atmospheric pressure or at slightly elevated pressure. The dehydrochlorination is effected by heating the chlorinated products for several hours at a temperature of between about 250° and 320° C. During the dehydrochlorination is it preferable to introduce a small amount of nitrogen and to admix several percent by weight of activated 65 carbon

The dehydrochlorination is most preferably effected at

2

a partial vacuum or at normal atmospheric pressure. It is also possible, however, to dehydrochlorinate at a slight superatmospheric pressure up to about 5 kg./sq. cm.

Suitable starting products for the process of the invention are all of the paraffins having more than 20 carbon atoms in the molecule, viz. synthetic paraffins as well as paraffins derived from the processing of petroleum.

The following examples are given by way of illustration and not limitation:

10

Example 1

A hard paraffin from the catalytic hydrogenation of carbon monoxide, containing the hydrocarbons boiling above 460° C. and having a setting point of 98° C. and an average number of carbon atoms of 48 was chlorinated at 120° C., while irradiating and stirring until 6 gram atoms of chlorine had been taken up per mole. The product obtained was then heated to 300° C. while passing through a stream of nitrogen. After heating for 5 hours, the content of the flask solidified. The product formed was insoluble in most solvents and could not be melted below a temperature of about 200° C. It showed elasticity to compression and was of caoutchouc-like character.

Example 2

Slab paraffin derived from petroleum, having a setting point of 52° C, and an average number of carbon atoms of 28 was treated with chlorine at 70° C. while stirring until 8 gram atoms of chlorine had been taken up per mole of hydrocarbon. The chlorinated product was heated to 300° C. while passing through a stream of nitrogen. After 8 hours the mass solidified. There was formed a product which would only melt with decomposition.

Example 3

C₂₂ hydrocarbons from the catalytic hydrogenation of carbon monoxide, the unsaturated portions of which had previously been hydrogenated were chlorinated at 60° C. while stirring until 10 gram atoms of chlorine had been taken up per mole. The chlorinated product was heated to 300° C. while passing through small amounts of nitrogen. After 8 hours, a product was obtained which melted at temperatures of above 200° C. with decomposition.

We claim:

- 1. Process for the production of rubber-like products from paraffin which comprises chlorinating a paraffin having more than 20 carbon atoms in the molecule with an amount of chlorine corresponding to at least 10 gram atoms of chlorine per mol of paraffin having about 22 carbon atoms in its molecule, at least 8 gram atoms of chlorine per mol of paraffin having about 28 carbon atoms in its molecule and at least 6 gram atoms of chlorine per mol of paraffin having about 48 carbon atoms in its molecule, thereafter dehydrochlorinating the chlorinated reaction product by heating to a temperature between about 250–320° C. for at least several hours and recovering the rubber-like product formed.
- 2. Process according to claim 1 in which said chlorination is effected in the presence of nitrogen.
- 3. A rubber-like paraffin product obtained by dehydrochlorinating a chlorinated paraffin having more than 20 carbon atoms in the molecule and 6-10 gram atoms of 65 chlorine per mol according to the process of claim 1.
 - 4. A rubber-like paraffin product obtained by dehydrochlorinating a chlorinated paraffin having about 22 car-

References Cited in the file of this patent bon atoms in the molecule and 10 gram atoms of chlorine per mol according to the process of claim 1. UNITED STATES PATENTS 5. A rubber-like paraffin product obtained by dehydro-chlorinating a chlorinated paraffin having about 28 carbon atoms in the molecule and 8 gram atoms of chlorine per 5 1,591,984 2,403,179 2,708,210 Krause et al. _____ July 13, 1926 Hull et al. _____ July 2, 1946 Sias _____ May 10, 1955 mol according to the process of claim 1. Kolling et al. _____ June 11, 1957 2,795,596 6. A rubber-like paraffin product obtained by dehydro-chlorinating a chlorinated paraffin having about 48 car-FOREIGN PATENTS bon atoms in the molecule and 6 gram atoms of chlorine Great Britain _____ May 12, 1939 505,898 per mol according to the process of claim 1. 10