Cl 260

Published July 13, 1943

Serial No. 374,605

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PREPARATION OF VALUABLE WAXES, RESINS, ARTIFICIAL SUBSTANCES, SOLVENTS AND SOFTENERS

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No Drawing. Application filed January 15, 1941

The group of waxes, resins, artificial substances, solvents and plasticifiers (softeners) chiefly includes the condensation- and polymerisation products, such as esters and ethers, which are obtainable in unlimited combinations from alcohols, aldehydes, ketones, carboxylic acids, especially high molecular fatty acids, or their derivatives respectively. As far as such substances or the basic substances necessary for their preparation are derived from natural sources, in particular from metabolic products of the animal or vegetable world, there is always the drawback that undesired protein compounds, glucosides, ferments or other additional compounds of unknown constitution and effect are also present.

The substances generally classified under waxes consist for example of esters of monobasic, high molecular fatty acids with principally high molecular monohydric alcohols, which do not belong to the glycerine series. Besides these esters and certain parts of free alcohol and free acids, they also contain glycerides which are easily decomposed under the influence of light and heat. The same is found in connection with the natural resins, softeners (plasticifiers) and solvents.

Since the impurities, even when there is only a trace of them, often produce undesired decompositions, their presence reduces the quality and durability of the final products obtained from natural raw materials. The undesired accompanying substances may, it is true, be removed by difficult and troublesome purifying processes, but these involve such great wastage that such methods are economically out of the question.

Besides undesired impurities, natural raw materials for the preparation of waxes, resins, artificial substances, solvents and plasticifiers have the disadvantage that on the one hand they are only available in limited quantities, and on the other hand it cannot be guaranteed that their composition and quality will always be uniform. Consequently, it has long been attempted to obtain the said substances by artificial means.

Two fundamental obstacles are met within the synthetic preparation of waxes, resins, and like substances.

In the first place the basic substances, which are directly required, such as high molecular alcohols, aldehydes or ketones, are difficult to obtain. In the present stage of technical development these substances are generally produced by working up or by decomposing suitable natural products, and thereby the disadvantages inherent in the natural products cannot be avoided.

In order to procure adequate and unlimited supplies of raw material it has already been attempted to prepare the high molecular oxygen compounds necessary for the synthesis (alcohols, aldehydes, ketones, carboxylic acids) by artificial means. But if, for example, in the preparation of waxes one starts with such intermediate products as are prepared synthetically with great difficulty, e. g. by the condensation of high molecular fatty acids with similarly prepared high molecular alcohols, the difficulty arises that such condensation products do not attain the good properties of natural products. The same difficulty is met with in the preparation of resins or resin-like substances, obtained from artificial resin alcohols, resin acids and resin esters. Also as regards the solvents and plasticifiers the synthetic products have not always been satisfactory. The same applies to the artificial substances.

These unfavorable properties of the said synthetic products are due to the fact that the artificial intermediate compounds used, e. g. high molecular alcohols, have no molecule-ramifications worth mentioning. But only from highly ramified basic synthesis substances can products be obtained which are strikingly similar to the natural substances. However, with the hitherto known methods, it is not possible to prepare sufficiently ramified intermediate products on scale for use in industry.

It has been found that oxygen containing carbon compounds, which are obtained when gas mixtures containing carbon oxide and hydrogen react in a catalytic way at a suitable temperature and under high pressure with carbon compounds having double or triple carbon bindings, are especially appropriate as a raw material for the synthetic preparation of waxes, resins, artificial substances, solvents and plasticifiers. When double bindings are present the watergas addition proceeds with an excellent yield between 50° C (122° F) and 200° C (392° F) and at 50–150 atm overpressure with metal catalysers, for example of the 8th group of the periodic system, in accordance with the following equations (R being an arbitrary organic compound-radical):

(1) $R.CH=CH.R+CO+H_2=R.CH_2—CH.R—CHO$

(2) $2R.CH=CH.R+CO+H_2$
$=R.CH_2—CH.R—CO—CH.R—CH_2.R$

Aldehydes and ketones are chiefly procured hereby. By a subsequent catalytic reduction which, for example, can be carried out at high pressure while using Fe-, Ni- or Co- contacts ac-

tivated with ThO_2, MgO or Al_2O_3, the corresponding alcohols can be easily obtained thereby. By means of suitable working-conditions one can, when using an excess of hydrogen, also prepare alcohols directly in a single process. The aldehydes and ketones, prepared by the addition of watergas, can also be easily converted into carboxylic acids by the usual methods of oxidation.

In such additions of watergas and reductions or oxidations respectively all the ramifications present in the basic hydrocarbon are retained. Moreover further ramifications are obtained, since the carbon oxide generally enters into the molecule as a side-chain and not at the end.

It is of special advantage to use the products of carbon oxide hydrogenation as basic alkenic substances for the above reactions. They can be prepared in any required quantity from watergas mixtures which are easily available everywhere. The highly alkenic dieseloil obtainable therefrom contains, for example, more than 60% isocompounds with highly ramified chains, and is a very satisfactory basic substance for the synthesis of the above mentioned substances.

Through repeated condensation of unsaturated particularly alkenic carbon bindings, a completely graduated sequence of molecules can be built up according to size. For this purpose the oxygen compounds obtained through the addition of watergas are first completely hydrogenated, then dehydrogenated to alkenes containing one carbon-atom more per molecule, whereupon watergas is again added to these alkenes. In this way all oxygen compounds in question (alcohols, aldehydes, ketones, carboxylic acids) can be obtained with good yields and by contact reactions which are very easily carried out in industry, so that the intermediate products with highly ramified molecules, which are required for the condensation of resins and artificial substances, are easily available. In this way, for example, normal propylic alcohol and isobutylic alcohol which at present are hardly obtainable, are easily available in any required quantity. Similarly, the corresponding alcohols, aldehydes, ketones and carboxylic acids can be obtained up to the highest molecular weights.

When using basic substances obtained in the manner described above, the preparation (condensation) of waxes, resins, artificial substances, solvents and plasticifiers is much more easily effected than by using natural raw materials or raw materials which have been artificially prepared in a different way.

For the preparation of valuable waxes, which may be used for example as roller masses, a substance for binding paint, or for impregnations, finishing textiles, rubbing masses and as basic substance of ointments, equimolecular quantities of a carboxylic acid containing 16 carbon atoms per molecule, prepared as described in the above, are, for example, condensed with an alcohol containing 14 carbon atoms per molecule. By heating sufficiently and stirring vigorously the reaction takes place without a hitch. The final product obtained has better properties than, for example, bees' wax.

The preparation of oxygen containing derivatives of aliphatic hydrocarbons which are applicable as solvents can be conducted in such a way that by choosing appropriate conditions during the conversion, alcohols (and from these alcohols, if desired ethers) are either obtained directly, or the oxygen containing compounds first procured are converted to alcohols by reduction. In the first case one treats, for example, alkenes containing one C-atom less than the desired alcohols, or corresponding mixtures, with carbonoxide and hydrogen at higher temperatures than are necessary for the preparation of oxocompounds, e. g. over 150° C (302° F) at approximately 100 atm in the presence of catalysers which contain as operating substances Fe, Ni or Co and as activating additions thorium-, magnesium- or aluminium oxide, and which may be brought upon carriers, such as infusorial earth.

For the preparation of ester-containing solvents, the alcohol mixture obtained is oxidised under mild conditions in such a way, that only a part of the alcohol is converted into acids, whereupon the mixture is esterified in a known way, if desired, after a previous isolation of the free fatty acids. However, the preparation of the fatty acids necessary for the esterification may also be performed apart from the preparation of alcohol by direct mild oxidation of a mixture of conversion products obtained by catalytic treatment with watergas at high pressures and temperatures of between 50° C (122° F) and 200° C (392° F). In this way very valuable solvents and plasticifiers are obtained when carboxylic acids with more than 10 carbon atoms are condensed with alcohols with more than 8 carbon atoms to the corresponding esters.

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