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(12) **Patent:**

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(54) PROCESS FOR THE SELECTIVE EXTRACTION OF OXYGENATED COMPOUNDS FROM PRIMARY PRODUCTS OF THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

(54) PROCEDE POUR L'EXTRACTION SELECTIVE DE COMPOSES OXYGENES DE PRODUITS PRIMAIRES DE L'HYDROGENATION CATALYTIQUE D'OXYDE DE CARBONE

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It is known that during the process of catalytic hydrogenation of carbon monoxide a number of by-products are formed, not only hydrocarbons but also oxygen-containing compounds, such for example as alcohols, aldehydes, acids, esters, ketones and acetals. When iron catalysts are used such oxygenated compounds are produced in particularly large quantities. Hydrocarbons and compounds containing oxygen are also formed during other chemical processes, for example during the reaction of water gas with unsaturated hydrocarbons, or during the oxidation of paraffins. Furthermore, hydrocarbon compounds of other origin sometimes contain oxygenated compounds in considerable quantities.

In many cases separation of the oxygen compounds is desirable, for they are frequently valuable by-products commanding high prices. In other cases the hydrocarbons in question cannot be used in further production processes, particularly where they are produced from carbon monoxide and hydrogen, if the compounds containing oxygen are not first removed.

It has already been suggested catalytically to convert the oxygen compounds or to destroy them in order to save the hydrocarbons for further processes. By such processes the valuable oxygen-containing compounds are lost which loss is considerable where large quantities of the oxygenated compounds are present.

Selective adsorption of the oxygenated compounds on activated silicic acid, alumina or other adsorption media has been attempted. Such processes have met with little success.

It has been found that oxygen-containing compounds may be satisfactorily separated in a simple manner from aliphatic hydrocarbons, particularly primary products obtained by the hydrogenation of carbon monoxide in the presence of an iron catalyst by selective extraction, if such hydrocarbon compounds are treated under the extraction conditions with liquid multi-valent alcohols, aromatic nitro-compounds and amino compounds or oxygen compounds of the furan group or of substitute compounds.

Suitable extractive media are for, example, glycol, glycerine, aniline, nitrobenzene, furfurol or their derivatives. Similar compounds can also be used. The compounds referred to and their derivatives only dissolve hydrocarbons to a small degree, whilst oxygen-containing compounds are adequately dissolved.

Particularly well suited for the extraction of oxygen-containing compounds from aliphatic hydrocarbons are multi-valent alcohols, as hydrocarbons are practically insoluble in multi-valent alcohols. Besides pure multivalent alcohols their derivatives can also be used, for example, monomethylglycol, dimethylglycol or trimethyleneglycol.

The selective effect of the extractive media of the invention may sometimes be improved by the addition of a small quantity of water, up to 10% of the solution.

If it is desired to extract large quantities of oxygen-containing compounds of high molecular weight from admixture with aliphatic hydrocarbons, the solvent power of multi-valent alcohols is sometimes inadequate. In such instances it is advantageous to add to the multi-valent alcohol, for example glycol, small quantities of alcohols of low molecular weight, for example methyl alcohol or ethyl alcohol. By such means the absorption capacity of the glycol for high molecular oxygen compounds is considerably increased. It is particularly advantageous to mix with the glycol a fraction of 50°C - 70°C boiling range obtained by fractionation of the products of the catalytic hydrogenation of carbon monoxide in the presence of iron or cobalt catalysts. This process has the advantage that for the extraction and working up of the oxygen-containing compounds - except the poly-hydroxy alcohols - no extraneous compounds beyond the multi-valent alcohols are used.

For carrying the process of the invention into effect, the hydrocarbon compounds to be treated are caused to flow through extraction towers arranged in cascade or series. The extraction towers are advantageously provided with suitable distributors in order to ensure adequate contact and mixture with the extraction substance. In this manner, from an aliphatic hydrocarbon mixture containing an OH figure of 90 - 100 and CO figure of 8 - 10 and containing small quantities of other oxygen compounds, all the oxygen products were extracted through a four-stage process to yield an end product at the last stage which did not show an OH figure or a CO figure. For the removal of the last traces of the multi-valent alcohols used as extraction media and the lower molecular weight alcohols that may have been added, for example methyl alcohol, a subsequent water treatment of the hydrocarbon compounds is advantageous.

The separation of the extracted oxygen-containing compounds from the extraction media such, for example, as glycol, is effected by simple distillation. In so far as no constant boiling azeotropic mixtures are formed, the single products are obtained directly in a state of high purity in the order of their boiling range. The oxygen-containing compounds lying above the boiling points of the extraction media, for example, above the boiling point of glycol, are advantageously separated by vacuum distillation in order to prevent decomposition and polymerization.

## EXAMPLE I.

Four extraction towers were arranged in series, each tower having a volume of 800 cc and being packed with Raschig rings of 5 mm diameter, and containing 700 cc of glycol. 200 cc per hour of the primary product of the catalytic hydrogenation of carbon monoxide were passed through the system. The hydrocarbon mixture had a boiling range of about 60°C and a final boiling point of about 500°C at atmospheric pressure. Its OH figure was 120. The hydrocarbon mixture was passed into each extraction tower through a distributor plate fixed at the base of the tower. Owing to its lower specific gravity it passed upwards through the glycol and was drawn off through an overflow pipe to pass to the next extraction stage. The hydrocarbon mixture from the first extraction tower still possessed an OH-figure of 24. After the second extraction stage this figure was OH-15. The hydrocarbon mixture from the last extraction tower had an OH-figure of about only 1 - 2.

## EXAMPLE 2

A two-stage extraction process had in each stage a volume of 800 cc and a filling of porous sintered plates ("Frittenplatten"). The first tower was filled with pure glycol, whilst the second tower contained a mixture of equal parts of glycol and methyl alcohol. 150 cc of the product of hydrogenation of carbon monoxide were passed through the extraction towers, the product having an OH-figure of 90 and an initial boiling point of 135°C. The hydrocarbon mixture was led into the lower part of the extraction tower and taken off from the upper part of the tower. The hydrocarbon mixture was washed with water after leaving the second extraction tower in order to remove the glycol and methyl alcohol. It then had an OH-figure of only 13.

## EXAMPLE 3

In known manner, an olefin-containing hydrocarbon fraction of 150° - 220°C boiling range obtained by the thermal cracking of petroleum, was added to water gas under super-atmospheric pressure and temperature in the presence of a cobalt catalyst. Subsequent hydrogenation converted the aldehyde produced with the same catalyst at a still higher temperature, into the corresponding alcohols. The end product so obtained contained 35% alcohols, 5% olefines and 60% saturated hydrocarbons.

For the extraction of the alcohols obtained the mixture was treated with the apparatus described in Example 1. The first extraction tower contained pure glycol, the second was filled with a mixture containing 2 parts of glycol and one part of methyl alcohol. The third tower was charged with a mixture that contained glycol and methyl alcohol in equal parts. The last tower contained water in order to remove the glycol and methyl alcohol from the treated mixture.

In this manner about 80% of the alcohols present were separated from the treated mixture and obtained in a practically pure state.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the selective extraction of oxygen-containing compounds from mixtures containing aliphatic hydrocarbons, particularly from the primary products of the hydrogenation of carbon monoxide, in the presence of iron catalysts, in which the hydrocarbon mixtures are acted upon with a compound which is liquid under the conditions prevailing during the process, said compound comprising at least one of a group consisting of multi-valent alcohols, aromatic nitro-compounds, aromatic amino-compounds, and oxygen compounds of the furan group, and their alkyl derivatives.

2. A process according to claim 1, in which alcohols of low molecular weight are used in admixture with the multi-valent alcohols.

3. A process according to claim 1 or claim 2 in which water is added to the multi-valent alcohols in an amount up to 10%.

4. A process according to claim 1 or 2 in which the extractive medium is diluted with an oxygen-containing fraction of boiling range 50°C. - 70°C. obtained from the reaction products of the hydrogenation of carbon monoxide over iron and cobalt catalysts.

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