[Second Edition.]

PATENT SPECIFICATION

Application Date: April 11, 1930. No. 11,522 / 30.

352,537

Complete Left: Oct. 4, 1930.

1254

Complete Accepted: July 13, 1931.

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Alcohols.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I.G. Farbenindustrie Aktiengesellschaft of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) to be as follows:—

By the oxidation of liquid or solid hydrocarbons, a mixture of different oxygen-containing products, such as acids, esters and the like which usually also contain unattacked initial material is generally obtained as the oxidation product.

My foreign correspondents have now found that a product consisting mainly of higher alcohols is readily obtained from the mixture produced in the manner already known by the oxidation of liquid or solid hydrocarbons, as for example in the liquid state with oxidising gases and the like with or without the employment of catalysts, by subjecting the said mixture obtained by oxidation, or constituents containing oxygen separated therefrom, such as esters, ketones and the like, to a hydrogenation under pressure with hydrogen or gases containing or supplying hydrogen. The hydrogenation is carried out with hydrogen at elevated pressures usually ranging up to about 100 atmospheres, in the presence of a hydrogenation catalyst, as for example finely divided metallic nickel and at elevated temperatures ranging from about 160° to 230° Centigrade, but higher or lower temperatures may also be employed. The absorption of hydrogen is completed in a short period of time. The duration of the reaction depends on the kind of the initial material and on the working conditions employed. For example with oxidation products from paraffin the hydrogenation effected at 200° Centigrade and under a pressure of 50 atmospheres in the presence of nickel as a catalyst is already completed in three hours. The separation of the alcohols formed from the unattacked initial material and any acids present may be effected in the manner already known by physical or chemical methods, as for example by the employment of solvents, by distillation or by esterification.

Alcohols having a more or less high melting point are obtained according to the nature of the initial materials employed for the oxidation, such as petroleum fractions, as for example middle oils, hard or soft paraffin and the like. For example, by employing hard paraffin as the initial material, a product is obtained the melting point of which is above 30° Centigrade.

The following Example will further illustrate the nature of this invention, but the invention is not restricted to this Example. The parts are by weight.

EXAMPLE.

700 parts of the neutral oxygen-containing constituents separated from an oxidation product obtained by treatment of hard paraffin wax with oxidising gases at a temperature of about 160° Centigrade and containing from about 35 to 40 per cent of oxygenated constituents having a neutral reaction, are treated for some hours in a stirring autoclave with hydrogen at 200° Centigrade under a pressure of 30 atmospheres in the presence of finely divided metallic nickel, and in this manner 5 parts of hydrogen are absorbed. The nickel catalyst is then filtered off. A pure white mixture consisting of higher wax alcohols is obtained and may be further purified by the usual methods, as for example by steam distillation. The mixture has hydrophilous properties and is eminently suitable for the preparation of ointments, esters, sulphonation products for wetting and cleansing agents and the like. The hydroxyl value of this mixture of alcohols amounts to from about 120 to 130.

Dated this 11th day of April, 1930.

J. Y. and G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C. 2,
Agents.

[*Price* 1*s*.]

Price 4s 6d.

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Alcohols.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I.G. Farbenindustrie Aktiengesellschaft of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

By the destructive oxidation of liquid or solid hydrocarbons, a mixture of different oxygen-containing products, such as acids, lactones, esters, aldehydes, ketones and the like which usually also contain unattacked initial material is generally obtained as the oxidation product.

My foreign correspondents have now found that products consisting mainly of the higher members of the aliphatic alcohol series are readily obtained from the mixture produced in the manner already known by the destructive oxidation of difficultly volatile, i.e. liquid or solid hydrocarbons in the liquid state as for example with gaseous oxidising agents containing free oxygen such as air or mixtures of oxygen with carbon dioxide or nitrogen, with or without the employment of catalysts, by subjecting the said mixture obtained by oxidation, or constituents containing oxygen separated therefrom, as for example the neutral fraction consisting of esters, ketones and the like, to a hydrogenation at superatmospheric pressure with large quantities of hydrogen, or gaseous mixtures containing hydrogen. The hydrogenation is carried out with hydrogen at elevated pressures usually ranging up to about 100 atmospheres in the presence of a hydrogenating catalyst, as for example finely divided metallic nickel, and at elevated temperatures ranging from about 150° to 230° Centigrade, but somewhat higher or lower temperatures such as up to about 250° and down to about 100° Centigrade may also be employed. The pressure employed should generally exceed 10 atmospheres since otherwise the reaction would proceed too slowly for practical purposes and pressures above 300 atmospheres are generally not employed since this method of working would require particularly costly apparatus. The absorption of hydrogen is completed in a short period of time. The duration of the reaction depends on the kind of the initial material and on the working conditions employed. For example with oxidation products from paraffin wax a hydrogenation effected at 200° Centigrade and at a pressure of 50 atmospheres in the presence of nickel as a catalyst is already completed in three hours. The separation of the alcohols formed from the unattacked initial material and any acids present may be effected in any usual and convenient manner by physical or chemical methods, as for example by the employment of solvents having a selective dissolving power, by distillation or by esterification.

Though the initial oxidation products are of a most heterogeneous composition the reduction stops against all expectation at the alcohol stage and practically no hydro-carbons are formed.

Alcohols having a more or less high melting point are obtained according to the nature of the initial materials employed for the oxidation, such as petroleum fractions boiling above 180° Centigrade, as for example middle oils, liquid hard or soft paraffins and the like, for example, by employing hard paraffin wax as the initial material in the oxidation, a product is obtained the melting point of which is above 30° Centigrade. In most cases mixtures of alcohols having a very high molecular weight are obtained, the alcohols from oxidation products of the middle oils containing an average of about 10 carbon atoms in the molecule and those from paraffin waxes an average of about 15 carbon atoms in the molecule. Depending on the content of the initial materials for the hydrogenation of unoxidised hydrocarbons the hydroxyl value of the final products will vary between 100 and 200.

The following examples will further illustrate how this invention may be carried out in practice, but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

700 parts of the neutral oxygen-containing constituents separated from an oxidation product obtained by treatment of hard paraffin wax with air at a temperature of about 160° Centigrade and containing from about 35 to 40 per cent of oxygenated constituents having a neutral reaction are treated for some hours in a stirring autoclave with hydrogen at 200° Centigrade under a pressure of 20 atmospheres in the presence of 3.5 parts

of finely divided metallic nickel, deposited on 10.5 parts of diatomaceous earth, and in this manner 5 parts of hydrogen are absorbed. The nickel catalyst is then filtered off. A pure white mixture consisting of higher wax alcohols is obtained and may be further purified by the usual methods, as for example by steam distillation. The mixture has hydrophilous properties and is eminently suitable for the preparations of ointments, esters, sulphonation products for wetting and cleansing agents and the like. The hydroxyl value of this mixture of alcohols amounts to from about 120 to 130.

EXAMPLE 2.

1000 parts of an oxidation product which has been prepared by blowing paraffin oil in the presence of 1 per cent of its weight of manganese naphthenate at 160° Centigrade with air and which contains about 35 per cent its weight of free carboxylic acids, are subjected in an autoclave and in the presence of 5 parts of nickel deposited on 15 parts of kieselguhr to the action of hydrogen at a temperature of 180° Centigrade for 4 hours while stirring after hydrogen has been forced into the autoclave until a pressure of 50 atmospheres has been attained. After filtering off the catalyst the last traces of nickel are washed out from the product by means of dilute aqueous sulphuric acid. After separating the saponifiable constituents of the products by a treatment with aqueous caustic soda at about 100° Centigrade and drawing off the aqueous soap solution, about 30 per cent of the original oxidation product is obtained as a mixture of high-molecular liquid alcohols which has a hydroxyl value of 160.

EXAMPLE 3.

1000 parts of an oxidation product prepared by blowing hard paraffin wax with air at about 160° Centigrade are treated with hydrogen at 250° Centigrade and 50 atmospheres pressure in an autoclave after adding 10 parts of finely divided cobalt which has been prepared by heating cobalt carbonate in a current of hydrogen at 350° Centigrade for 36 hours. After filtering off the catalyst the product is washed with dilute aqueous sulphuric acid for removing traces of cobalt from the reaction product. After separating saponifiable constituents (free acids, lactones and esters) from the reaction product a semi-solid mixture of alcohols is obtained in a yield of 65 per cent of the original oxidation product, which may find useful application in the production of salves or ointments or for the production of wetting, cleansing or emulsifying agents by sulphonation.

By the aforedescribed treatment 40 per cent by weight of the esters and free acids contained in the oxidation product are converted into alcohols as will be seen from the following figures:

	Acid value	Saponification value	Unsaponifiable matter (per cent)	Hydroxyl value of unsaponifiable matter
Initial material –	78.5	143.3	47.0	25.3
Reaction product –	13.5	64.6	65.2	104.8

EXAMPLE 4.

1000 parts of an oxidation product prepared by blowing soft paraffin wax at about 150° Centigrade with air from which free carboxylic acids have been removed with the aid of aqueous soda solution, are mixed with 5 parts of nickel deposited on 15 parts of kieselguhr and the whole is then heated for four hours at 200° Centigrade in an autoclave while stirring after hydrogen has been forced into the latter until a pressure of 60 atmospheres is attained. The nickel catalyst is then filtered off and after separating the saponifiable constituents (esters, lactones and acids) a mixture of semi-solid high molecular alcohols is obtained which possesses a hydroxyl value of 140.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the manufacture and production of products consisting mainly of the higher members of the aliphatic alcohol series which comprises heating the products, obtained by the destructive oxidation of difficultly volatile hydrocarbons in the liquid state by means of gaseous oxidising agents containing free oxygen, or a fraction of such oxidation products in the presence of large quantities of hydrogen and of a hydrogenating catalyst at a pressure above atmospheric pressure.

2. The process for the manufacture and production of products consisting mainly

of the higher members of the aliphatic alcohol series substantially as described in each of the foregoing Examples.

3. Products consisting mainly of the higher members of the aliphatic alcohol series when prepared in accordance with the preceding claiming clauses.

Dated this 4th day of October, 1930.

J. Y. and G. W. JOHNSON,
47, Lincoln's Inn Fields,
London, W.C. 2,
Agents.

Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 123A.—50/11/1931.]

NO