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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in the Manufacture and Production of Organic Acids

I, George William 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 organised under the Laws of Germany) to be as follows:—

For the production of carboxylic acids it has been proposed, inter alia, to oxidise high molecular weight non-aromatic compounds and to acidify the saponified oxidation products, if necessary after the separation of unsaponified constituents, with mineral acids, such as sulphuric acid, hydrochloric acid or nitric acid.

My foreign correspondents have now found that from the saponification products of oxidation products of high molecular weight non-aromatic compounds, the acids can be obtained in a manner which is of special advantage industrially by causing sulphur dioxide or watersoluble bisulphites to act on the saponification products in the presence of water, the free organic acids thus separated being then removed from the aqueous solution.

As initial materials for the said process there may be mentioned the oxidation products of hard or soft paraffin wax, paraffin oil, middle oils, hydrogenation products of coals, tars, oxides of carbon, and also of waxes, oils, fats and the like obtained in known manner and which may be saponified for example with alkalies, ammonia or amines. The unsaponified constituents are preferably removed before the treatment with sulphur dioxide or bisulphites.

As watersoluble bisulphites there may be mentioned for example sodium, potassium, calcium or ammonium bisulphite. It is preferable to work under such conditions, in particular as regards temperature, that the saponification products are present in dissolved form and the acids separated therefrom are liquid, because in this way both the splitting of the soaps and the separation of the fatty acids from the aqueous solution can be readily carried out.

The process may be carried out under any pressure and if desired in continuous operation. When watersoluble saponification products are present, it is preferable to work in aqueous solution; saponification products which are insoluble in water, as for example calcium soaps, are preferably worked up in aqueous suspension or dispersion. The amount of bisulphite or sulphur dioxide used should generally speaking be sufficient for the complete splitting of the saponification products; it is preferable to use a certain excess. The splitting of the saponification products may also be carried out in two or more stages, sulphur dioxide or bisulphites being used in all stages, or only in certain stages while other splitting agents are used in other stages.

The sulphite solutions obtained after the separation of the fatty acids may be converted into bisulphite by leading in sulphur dioxide and then used again for the splitting of saponification products. It is very suitable to wash gas mixtures containing sulphur dioxide with the used bisulphite solutions, the latter thereby being regenerated. Gas mixtures which, in addition to inert gases, contain only relatively small amounts of sulphur dioxide and which are therefore less suitable as such for the direct splitting of saponification products chiefly because when they are led into the aqueous solution of the saponification products they cause undesirable foaming, can thus be rendered directly utilisable for the said purpose.

The use of sulphurous acid or bisulphites instead of the usual mineral acids hitherto employed for the splitting of saponification products of paraffin oxidation products has the advantage that the exhausted solutions after use can be regenerated again very easily by treatment with industrial waste gases containing sulphur dioxide, even those having but a small content of sulphur dioxide. Furthermore, the basic substances used for the saponification, such as alkalies, alkaline earths or ammonia, are recovered in the form of valuable salts, as for example alkali sulphites or bisulphites which are required industrially, as for example in the cellulose industry.

The salts of lower fatty acids, as for example acetic, propionic, butyric acids and the like, contained in the saponification products become enriched in the bisulphite solutions used. As soon as a sufficient enrichment in such salts is reached, these acids may also be recovered by evaporating a part of the bisulphite solution and setting the fatty acids free from their salts by acidification, for example with sulphuric acid, and then recovering them in the usual way.

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

Example 1.

A product obtained by the oxidation of hard paraffin wax with air is saponified with caustic soda solution or saturated soda solution and freed from unsaponified constituents. Into the aqueous soap solution sulphur dioxide is led at 60° Centigrade until the fatty acids are completely separated. Two layers are formed; the upper layer contains the fatty acids and the lower layer consists of an aqueous solution of sodium sulphite and bisulphite. The two layers are separated from each other and further worked up in the usual manner.

Example 2.

15 parts of a 35 per cent. sodium bisulphite solution are added while stirring at 70° Centigrade to 20 parts of an aqueous 50 per cent. crude soap solution obtained from a paraffin oxidation product. The free acids which separate as the upper layer are separated and washed. About 8 parts of acids of pale colour are thus obtained, the acid value being 225. The aqueous solution containing sodium sulphite is concentrated to such an extent that after cooling about half of the sodium sulphite formed crystallises out. After separating the same, the mother liquor is treated with sulphur dioxide or gases containing the same, whereby sodium bisulphite is formed which may be used for the splitting of saponification products.

Example 3.

A 40 per cent. soap solution (obtained from a paraffin obtained by reduction of carbon monoxide with hydrogen by oxidation with air and neutralisation with caustic soda solution) are led continuously into a tower 6 metres in height and 150 millimetres in diameter which is filled with Raschig rings at 80° Centigrade at a point 1.5 metres from the bottom, while at the same time a sodium bisulphite solution (specific gravity 1.3) flows down from the top. The bisulphite solution reacts with the soap solution with the formation of free carboxylic acids, which are withdrawn from the upper part of the tower. The used bisulphite solution collects in the lower part of the tower; it is supplied to a washing tower in which it is regenerated to sodium bisulphite solution with gases containing from 4 to 5 per cent. of sulphur dioxide. About half of the regenerated bisulphite solution, after use for splitting, is continuously worked up to solid sodium sulphite or exploited in another way.

The free carboxylic acids obtained may if necessary be subjected to an aftertreatment with a bisulphite solution or with gases containing sulphur dioxide or with mineral acids in order to convert small amounts of unsplit saponification products still present into free carboxylic acids; they are then washed with water.

Example 4.

A gas mixture containing 6 per cent. of sulphur dioxide is led into a vessel containing a solid calcium soap having a water content of about 70 per cent. obtained from an oxidation product of hard paraffin wax. A separation into water and calcium soap thus takes place. By stirring or suitable supply of gas, an aqueous suspension of the calcium soap is produced which is then treated with the gas mixture containing sulphur dioxide until the free carboxylic acids have separated from the calcium soap. There is thus obtained for example a mixture of carboxylic acids having an acid value of 220 and also a calcium bisulphite solution. By boiling the latter, the sulphur dioxide can be partly expelled whereby calcium sulphite is precipitated in the solid form.

Dated this 11th day of November, 1937.

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

COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of Organic Acids

I, George William 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 organised 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:—

The recovery of carboxylic acids from oxidation products of high-molecular aliphatic compounds is usually effected by acidifying the saponified oxidation products, if necessary after the separation of unsaponified constituents, with mineral acids, such as sulphuric acid, hydrochloric acid or nitric acid.

My foreign correspondents have now found that from the saponification products of oxidation products of high molecular weight aliphatic compounds, the acids can be obtained in a manner which is of special advantage industrially by causing sulphur dioxide or watersoluble bisulphites to act on the saponification products in the presence of water, the free organic acids thus separated being then removed from the aqueous solution.

As initial materials for the said process there may be mentioned the oxidation products of hard or soft paraffin wax, paraffin oil, middle oils, hydrogenation products of coals, tars, oxides of carbon, and also of waxes, oils, fats and the like obtained in known manner and which may be saponified for example with alkalies, ammonia or amines. The unsaponified constituents are preferably removed before the treatment with sulphur dioxide or bisulphites.

As watersoluble bisulphites there may be mentioned for example sodium, potassium, calcium or ammonium bisulphite. It is preferable to work under such conditions, in particular as regards temperature, that the saponification products are present in dissolved form and the acids separated therefrom are liquid, because in this way both the splitting of the soaps and the separation of the fatty acids from the aqueous solution can be readily carried out.

The process may be carried out under any pressure at normal or moderately elevated temperatures, for example between 40° and 90° Centigrade and if desired in continuous operation. The bisulphite solutions may be employed in a not too greatly diluted form, bisulphite solutions from 10 to 35 per cent. strength preferably being used. When the saponification products are soluble in water it is preferable to work in aqueous solution; saponification products which are insoluble in water, as for example calcium soaps, are preferably worked up in aqueous suspension or dispersion. The amount of bisulphite or sulphur dioxide used should generally speaking be sufficient for the complete splitting of the saponification products; it is preferable to use a certain excess. The splitting of the saponification products may also be carried out in two or more stages, sulphur dioxide or bisulphites being used in all stages, or only in certain stages while other splitting agents such as hydrochloric or sulphuric acid are used in other stages.

The sulphite solutions obtained after the separation of the fatty acids may be converted into bisulphite by leading in sulphur dioxide and then used again for the splitting of saponification products. It is very advantageous to wash gas mixtures containing sulphur dioxide with the used bisulphite solutions, the latter thereby being regenerated. Gas mixtures which, in addition to inert gases, contain only relatively small amounts of sulphur dioxide and which are therefore less suitable as such for the direct splitting of saponification products chiefly because when they are led into the aqueous solution of the saponification products they cause undesirable foaming, can thus be rendered directly utilisable for the said purpose.

The use of sulphurous acid or bisulphites instead of the usual mineral acids hitherto employed for the splitting of saponification products of paraffin oxidation products has the advantage that the exhausted solutions after use can be regenerated again very easily by treatment with industrial waste gases containing sulphur dioxide, even those having but a small content of sulphur dioxide. Furthermore, the basic substances used for the saponification, such as alkalies, alkaline earths or ammonia, are recovered in the form of valuable salts, as for example alkali metal sulphites or bisulphites which are required industrially, as for example in the cellulose industry.

The salts of lower fatty acids, as for example acetic, propionic, butyric acids and the like, contained in the saponification products become enriched in the bisulphite solutions used. As soon as a sufficient enrichment in such salts is reached, these acids may also be recovered by evaporating a part of the bisulphite solution and setting the fatty acids free from their salts by acidification, for example with sulphuric acid, and then recovering them in the usual way.

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

EXAMPLE 1.

A product obtained by the oxidation of hard paraffin wax with air is saponified with caustic soda solution or saturated soda solution and freed from unsaponified constituents. Into the aqueous soap solution sulphur dioxide is led at 60° Centigrade until the fatty acids are completely separated. Two layers are formed; the upper layer contains the fatty acids and the lower layer consists of an aqueous solution of sodium sulphite and bisulphite. The two layers are separated from each other and further worked up in the usual manner.

EXAMPLE 2.

15 parts of a 35 per cent. sodium bisulphite solution are added while stirring at 70° Centigrade to 20 parts of an aqueous 50 per cent. crude soap solution obtained from a paraffin oxidation product. The free acids which separate as the upper layer are separated and washed. About 8 parts of acids of pale colour are thus obtained, the acid value being 225. The aqueous solution containing sodium sulphite is concentrated to such an extent that after cooling about half of the sodium sulphite formed crystallises out. After separating the same, the mother liquor is treated with sulphur dioxide or gases containing the same, whereby sodium bisulphite is formed which may be used for the splitting of saponification products.

EXAMPLE 3.

A 40 per cent. soap solution (obtained from a paraffin obtained by reduction of carbon monoxide with hydrogen by oxidation with air and neutralisation with caustic soda solution) are led continuously into a tower 6 metres in height and 150 millimetres in diameter which is filled with Raschig rings at 80° Centigrade at a point 1.5 metres from the bottom, while at the same time a sodium bisulphite solution (specific gravity 1.3) flows down from the top. The bisulphite solution reacts with the soap solution with the formation of free carboxylic acids, which are withdrawn from the upper part of the tower. The used bisulphite solution collects in the lower part of the tower; it is supplied to a washing tower in which it is regenerated to sodium bisulphite solution with gases containing from 4 to 5 per cent. of sulphur dioxide. About half of the regenerated bisulphite solution, after use for splitting, is continuously worked up to solid sodium sulphite or exploited in another way.

The free carboxylic acids obtained may if necessary be subjected to an aftertreatment with a bisulphite solution or with gases containing sulphur dioxide or with mineral acids in order to convert small amounts of unsplit saponification products still present into free carboxylic acids; they are then washed with water.

EXAMPLE 4.

A gas mixture containing 6 per cent. of sulphur dioxide is led into a vessel containing a solid calcium soap having a water content of about 70 per cent. obtained from an oxidation product of hard paraffin wax. A separation into water and calcium soap thus takes place. By stirring or suitable supply of gas, an aqueous suspension of the calcium soap is produced which is then treated with the gas mixture containing sulphur dioxide until the free carboxylic acids have separated from the calcium soap. There is thus obtained for example a mixture of carboxylic acids having an acid value of 220 and also a calcium bisulphite solution. By boiling the latter, the sulphur dioxide can be partly expelled whereby calcium sulphite is precipitated in the solid form.

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 organic acids from oxidation products of high molecular aliphatic compounds, which comprises causing sulphur dioxide or watersoluble bisulphites to act on the saponified oxidation products after removing the unsaponifiable constituents in the presence of water and withdrawing the carboxylic acids separated from the aqueous solution.

2. In the process as claimed in claim 1, employing sulphur dioxide and watersoluble bisulphites to act subsequently in several stages on the saponified oxidation products after removing the unsaponifiable constituents.

3. In the process as claimed in claim 1, leading sulphur dioxide into the aqueous sulphite-containing solution obtained thus converting the sulphite into bisulphite and employing the bisulphite solution thus obtained for splitting another batch of saponified oxidation products.

4. The process for the manufacture and production of organic acids from oxidation products of high-molecular aliphatic compounds substantially as described in each of the foregoing Examples.

5. Organic acids from oxidation pro-

ducts of high-molecular aliphatic compounds when obtained according to the process particularly described and ascertained.

Dated this 12th day of September, 1938.
J. Y. & G. W. JOHNSON,
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Agents.

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