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COMPLETE SPECIFICATION.

Process for the oxidation of paraffinic hydrocarbons

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German joint-stock corporation, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The invention relates to a process for the oxidation of paraffinic hydrocarbons.

The oxidation of paraffinic hydrocarbons by means of nitrous gases in the presence of nitro-sulphuric acid is known. The oxidising agent may, for example, be the gases produced in the combustion or oxidation of ammonia, which, in the presence of concentrated sulphuric acid (96%H_2SO_4) or of concentrated nitro-sulphuric acid, act upon the hydrocarbons. The advantage of this method is that, together with monocarboxylic acids, only very small quantities of nitrogen-containing compounds are produced.

By the terms "nitrous gas" and "nitrous gases", as used throughout the specification and the appended claims, are to be understood gases which contain NO and/or NO_2. The term "nitro-sulphuric acid", as used throughout the specification and the appended claims, is to be understood to mean sulphuric acid in which NO and NO_2 are dissolved.

When the diesel oil fraction, boiling between 250°C. and 320°C. and containing C_{14}-C_{18} hydrocarbons, which is obtained from the products of the catalytic hydrogenation of carbon monoxide, is oxidised with a gas mixture containing about 10% NO_2, such as is obtained in the catalytic oxidation of ammonia, reaction products are produced having an acid value or acid number of about 50 and an ester value or ester number of about 100, if the oxidation is carried out for a period of twelve hours at a temperature of 120°C. with the use of 1,000 litres of nitrous gases per kilogram of diesel oil per hour. If, under otherwise similar conditions, for every kilogram of diesel oil, 500 ccms. of a 96% sulphuric acid previously loaded with gases containing NO_2 are simultaneously used, then the reaction products obtained, also have an acid number of 50, but their ester number is only 5. The limited extent of the resultant oxidation effect, expressed by the low acid number, is a disadvantage of this method of paraffin oxidation.

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It has now been found that an appreciable increase in the oxidation effect occurs, if, instead of using a highly concentrated sulphuric acid of this kind, nitro-sulphuric acid having an H_2SO_4 content of less than 90% and preferably having a content of from 70% to 90% H_2SO_4, is used. Acids containing 80% to 90% H_2SO_4 give particularly good results.

In the process according to the invention, in spite of a sharp increase in the acid number, that is to say, in spite of an appreciably more intense oxidation, the ester number remains considerably below the value obtained when operating without sulphuric acid.

If the above mentioned diesel oil fraction obtained from the products of the catalytic hydrogenation of carbon monoxide, is converted with a gas mixture containing 10% NO_2, 1,000 litres of this gas per kilogram of the diesel oil fraction being passed through per hour for a period of twelve hours at a temperature of 120°C., then the following results are obtained:—

Nitro-sulphuric acid used			
Density (D_{20})	H_2SO_4 % by wt.	Acid No.	Ester No.
1.9	96	50	5
1.8	85	100	20
1.7	76	135	35
1.6	69	150	60
1.5	60	140	90
1.4	50	120	120

These figures show that even with an H_2SO_4 concentration of 85% the formation of fatty acid is twice as high as with the 96% nitro-sulphuric acid hitherto used. Maximum oxidation is attained with an acid concentra-

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tion of about 69% H_2SO_4, a product having an acid number of 150 being obtained. When the sulphuric acid concentration falls below about 69%, the acid number of the product diminishes.

The ester number also increases as the sulphuric acid concentration falls; at the maximum fatty acid formation, that is to say with a sulphuric acid concentration of 69%, the ester number attains a value of 60. Although, under these conditions, the oxidation effect is some three times as great as when the oxidation is carried out without the addition of sulphuric acid, the ester number is only about half as high. With a sulphuric acid concentration below 69% H_2SO_4, the ester number shows further increase. It is therefore advantageous to use a sulphuric acid containing not less than 69% H_2SO_4 and not more than 90% H_2SO_4.

The ester number obtained for the resultant reaction product is dependent upon the presence of nitro-paraffins in the reaction product, since nitro-paraffins react with the KOH solution used in the estimation of the ester number. In the oxidation by means of nitro-sulphuric acid of a concentration according to the invention, larger quantities of nitro-paraffins will be produced as a by-product. This is, however, not of importance, since, by saponification of the reaction mixture, which can be carried out by means of alkali carbonates, for example, a solution of sodium carbonate, the nitro-paraffins, together with the unchanged hydrocarbons, can be easily separated. A separation into layers occurs upon saponification, the unreacted hydrocarbons and the nitro-paraffins separating out in a layer above the sodium carbonate solution. The mixture of fatty acids which is obtained from the aqueous sodium carbonate layer upon treatment with mineral acids, shows practically no ester number.

If the unreacted hydrocarbons and the nitro-paraffins obtained in the upper layer are again oxidised, then the result depends upon the concentration of the nitro-sulphuric acid used. If dilute nitro-sulphuric acid is used, a further increase in the ester number generally occurs. When nitro-sulphuric acid containing 80%-90% H_2SO_4 is used in the further oxidation of the separated hydrocarbon/nitro-paraffin mixture, it is found, somewhat surprisingly, that no further rise in the ester number occurs. If such acid concentrations are used in a process in which the hydrocarbons which have escaped oxidation are recycled, no loss of yield can occur through the further formation of nitro-compounds.

The mixture of nitro-paraffins and unreacted hydrocarbons which separates upon treatment with sodium carbonate solution is preferably recycled to the process, not alone, but in admixture with an appropriate amount of fresh hydrocarbons. The amount of added, fresh hydrocarbons is governed by the quantity of fatty acids produced in the oxidation. By the use of nitro-sulphuric acids the concentration of which lies between 80%-90% H_2SO_4, acid numbers may be obtained which are roughly twice as high as when highly concentrated nitro-sulphuric acids are used, without the formation of nitro-paraffins as by-products upon return of the unconverted hydrocarbons to the process.

Since water occurs as a by-product of the oxidation of the hydrocarbons, steps must be taken to maintain the concentration of the sulphuric acid. For this purpose, the water produced can continuously be wholly or partially separated outside the reaction zone, from the reaction gases used in the process, by methods which are well known. Instead of this, the moisture content of the gas or the rate of flow of the gas may be altered. Finally, it is also possible to obtain a constant acid concentration by varying the amount of acid added, in such a way that, as the amount of water increases, so the quantity of acid present in the reaction zone is increased.

If, during the oxidation, a constant concentration of nitro-sulphuric acid is maintained, then the acid may be constantly re-used. A previous treatment of the used acid with nitrous gases is not then necessary, since the NO_2 content of the used acid is dependent only upon the acid concentration, and, when fresh sulphuric acid is used, regains its former end value a short time after the beginning of the reaction. With the comparatively large quantities of sulphuric acid needed for the oxidation of paraffins, according to the invention, it is of particular advantage that the nitro-sulphuric acid can be continuously recycled.

The process hitherto described of carrying out the oxidation of paraffins according to the invention has the disadvantage that the small quantities of nitrous oxide (N_2O) and nitrogen (N_2), which are produced in secondary reactions, remain in the recycle gas and dilute it. In order to maintain the NO_2 concentration at a level sufficient for the oxidation of the paraffins, a certain proportion of the recycle gas is continuously or intermittently withdrawn from the cycle and replaced by fresh gas. This procedure results in an increase in the consumption of NO_2, since the part of the NO_2 introduced is lost in the less valuable, nitrogen-rich gases which are withdrawn. The gases withdrawn are also contaminated by organic compounds and cannot be used again until they have been thoroughly purified.

These disadvantages may be avoided if the oxidation of the paraffinic hydrocarbons is effected by nitro-sulphuric acid alone, without the use of the nitrous gases, the nitro-sulphuric acid containing less than 90% H_2SO_4. The paraffins can then be converted to fatty acids without prejudice to the extent of the main conversion. Since large quantities of the nitro-sulphuric acid are necessary for the oxidation, the sulphuric acid is introduced into the cycle between the paraffin oxidation chamber and an apparatus by means of which the NO_2 content of recycled sulphuric acid may again be increased.

Even when nitro-sulphuric acid is used exclusively, the degree of oxidation and the formation of nitro-paraffins are also influenced to a certain extent by the concentration of the sulphuric acid introduced. The best results are obtained with a nitro-sulphuric acid which contains 80% to 85% H_2SO_4.

In carrying out the oxidation of the paraffins, such quantities of nitro-sulphuric acid are continually passed into a reaction chamber filled with liquid or molten paraffin hydrocarbons that a sufficient quantity of nitrogen dioxide is available for the oxidation. During the oxidation, a part of the NO_2 dissolved in the sulphuric acid is reduced and escapes from the sulphuric acid in the form of NO. The acid passing out of the reaction chamber therefore contains a smaller quantity of nitrous gases than the acid flowing into the chamber. To increase the concentration of nitrous gases in the acid, the acid withdrawn from the reaction chamber is passed downwardly through a column in contercurrent to a stream of nitrous gases. In this way the NO_2 concentration of the sulphuric acid is restored, whereupon it may be recycled to the reaction chamber. For loading the sulphuric acid, nitrous gases of varied origin are suitable. It is possible to use nitrous gases with so low a concentration of NO_2 that they could not, hitherto, be used for the oxidation of paraffins. The nitrous gases escaping from the reaction chamber are also passed into the column used for loading the sulphuric acid; purely mechanical losses of nitrous compounds are thereby avoided.

The water produced in the reaction may be removed by heating the acid withdrawn from the reaction chamber before it is passed to the column to be reloaded with nitrous gases. It is, however, considerably simpler to pass into the paraffin oxidation chamber such a quantity of dry gas that the water formed may be removed, more or less completely, by the gas. For such purposes, inert gases as well as gases containing oxygen, for example air, are suitable. The gas, after passing through the reaction chamber, is freed by cooling from its content of water vapour. The gases used to remove the water may then be passed through the sulphuric acid column.

The gas serving to remove the water can be brought into the process cycle because, during the reaction, the gas also extracts small quantities of nitrous compounds from the sulphuric acid. If it were not recycled, it would be necessary to pass all the gas serving to carry off the water through the column in which the sulphuric acid is loaded with nitrous gases. If the gas carrying off the water is recycled, there need pass through the sulphuric acid column only that quantity of the gas which corresponds to the amount of nitrous gases given off by the acid. In any case, the gases passed into the sulphuric acid column must contain sufficient oxygen to enable the NO formed in the reaction to be oxidised to NO_2.

The advantages of carrying out the process of the invention in this way, working only with nitro-sulphuric acid, consists in that the oxidation of the paraffins may be effected with nitrous gases in which the concentration of NO_2 is relatively low. The N_2O and N_2 formed during the reaction can be removed, without loss of NO_2, along with the gases passing from the reaction chamber which give up their nitrous compounds to the sulphuric acid. The waste gas escaping overhead from the sulphuric acid column consists almost entirely of N_2 and N_2O, which gas is of no value for the oxidation of paraffins. Only such quantity of fresh nitrous gas needs to be continuously introduced into the process as is lost by reduction to nitrogen or nitrous oxide.

The process according to the invention may be used with particular advantage for all paraffinic hydrocarbons having more than ten carbon atoms in the molecule; it is particularly applicable in the treatment of hydrocarbons obtained by the catalytic hydrogenation of carbon monoxide because these are preponderantly aliphatic hydrocarbons.

Example I

The fact that, in the process for the oxidation of paraffins according to the invention, no excessive increase in the ester number occurs, was demonstrated as follows:—

A hydrogenated diesel oil fraction boiling within the range 250°C.-300°C., containing C_{14}-C_{18} hydrocarbons and obtained from the products of the catalytic hydrogenation of carbon monoxide, was oxidised at a temperature of 120°C. by means of nitrous gases in the presence of nitro-sulphuric acid containing 83% H_2SO_4. The oxidation product obtained had an acid number of 105 and an ester number of 24. It was saponified with dilute sodium carbonate solution upon which a separation into layers occurred. The layer above the aqueous phase contained a mixture of the unchanged hydrocarbons and the nitrogen-containing compounds produced during the oxidation.

This mixture gave an acid number of 2 and an ester number of 37. 1,000 gms. of this mixture were treated, in a glass flask, with 500 ccms. of an 85% sulphuric acid which, after absorption of about 10% by weight of NO_2, had a density of 1.8. The mixture was heated to 120°C. after which 1,000 litres per hour of a nitrous gas/air mixture were passed through with constant stirring. The mixture of nitrous gas and air was saturated with water vapour at 20°C., and contained 10% by volume of NO_2. The water carried off with the exit gases was condensed in a connected cooler and drawn-off, while the organic constituents carried off, and also condensed, were returned to the reaction flask. After a reaction time of 12 hours, the reaction was interrupted, and the oxidation product washed with hot water. 840 gms. of a pale yellow liquid product were obtained, the acid number of which was 103 and the ester number 36. Compared with the hydrocarbon mixture introduced, the ester number thus remained practically unchanged.

When 1,000 gms. of the hydrocarbon mixture used above were oxidised under the same conditions, but using a sulphuric acid charged with about 10% by weight of NO_2 and containing 73% H_2SO_4, then 830 gms. of a yellow-coloured, liquid oxidation product with an acid number of 142 and an ester number of 73, were obtained. In this case, therefore, an appreciable increase in the ester number occurred.

Example 2

In a glass flask, the base of which is provided with a discharge cock, 1,000 gms. of a hard paraffin wax (average molecular weight 496) obtained by the catalytic hydrogenation of carbon monoxide, were heated to 120°C.-125°C. with constant stirring. By means of a dropping funnel, 700 ccms. of nitro-sulphuric acid containing 83% H_2SO_4 were added hourly. An equal quantity of acid was continually drawn-off from the base of the flask. Air was passed through the liquid reaction mixture at the rate of 600 litres per hour. The exit gas from the glass flask, which gas contained the NO freed from the sulphuric acid as well as the N_2 and N_2O formed in the oxidation, was passed upwardly through a column in countercurrent to the sulphuric acid withdrawn from the base of the flask. The gas escaping from the head of the column was free from NO_2 and NO.

A further 150 litres of a gas mixture containing 15% NO_2 were also introduced per hour into the column to replace the NO_2 and reduced to N_2O and N_2. Thus 22.5 litres of NO_2 were added per hour.

After a reaction time of 10 hours, the oxidation was interrupted and the reaction mixture washed with hot water to free it from sulphuric acid. A product was obtained with a neutralization number of 79 and a saponification number of 89. The sulphuric acid can be used for further conversions.

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

1. A process for the oxidation of paraffinic hydrocarbons, which comprises treating the paraffinic hydrocarbons with nitrous gases and nitro-sulphuric acid containing less than 90% H_2SO_4.

2. A process according to claim 1, in which the nitro-sulphuric acid contains not less than 70% H_2SO_4.

3. A process according to claim 1, or claim 2, in which the concentration of the nitro-sulphuric acid is maintained substantially constant during the oxidation of the paraffinic hydrocarbons.

4. A process according to any one of claims 1 to 3, in which the nitrous gases entering the oxidation zone are substantially free from water vapour.

5. A process according to any one of claims 1 to 4, in which the reaction gases introduced into the process are wholly or partly freed of their water vapour content outside the oxidation zone.

6. A process according to any one of claims 1 to 5, in which the rate of flow of the gases and/or the amount of added nitro-sulphuric acid is increased, if there is an increase in the quantity of water in the oxidation zone.

7. A process according to any one of claims 1 to 6, in which nitro-paraffins and unconverted hydrocarbons are separated from the oxidation product by treatment with alkali-metal carbonates and are subjected to a further oxidation treatment with a nitro-sulphuric acid which contains 80%-90% H_2SO_4.

8. A process according to claim 7, in which the nitro-paraffins and unconverted hydrocarbons are admixed with fresh hydrocarbons before further oxidation.

9. A process according to claim 1, in which a sulphuric acid containing less than 90% H_2SO_4 and dissolved nitrogen dioxide to an extent sufficient to avoid the use of the nitrous gases, is used in the oxidation without nitrous gases.

10. A process according to claim 9, in which the nitro-sulphuric acid contains from 80% to 85% H_2SO_4.

11. A process according to claim 9 or claim 10, in which the nitro-sulphuric acid is continuously withdrawn from the oxidation zone, to be recharged with nitrogen dioxide and is then recycled to the oxidation zone.

12. A process according to any one of claims 8 to 10, in which the acid withdrawn from the oxidation zone is heated to remove the reaction water absorbed during the oxidation, before it is recharged with nitrogen dioxide.

13. A process according to any one of claims 9 to 12, in which a dry gas is passed through the reaction mass to remove reaction water formed during the oxidation.

14. A process according to claim 13, in

which the gas used to remove reaction water is dried after passing through the oxidation zone, such a proportion of the gas as corresponds to the quantity of nitrous gases given off by the nitro-sulphuric acid in the oxidation zone being then passed through the nitro-sulphuric acid withdrawn from the oxidation zone whilst the remainder of the gas is recycled to the oxidation zone.

15. A process according to any one of the preceding claims, in which the paraffinic hydrocarbons contain more than ten carbon atoms in the molecule.

16. A process for the oxidation of paraffinic hydrocarbons, substantially as hereinbefore described with reference to Example 1 of the specification herein.

17. A process for the oxidation of paraffinic hydrocarbons, substantially as hereinbefore described with reference to Example 2 of the specification herein.

18. A process for the oxidation of paraffinic hydrocarbons with nitrous gases and nitro-sulphuric acid, substantially as hereinbefore described.

19. A process for the oxidation of paraffinic hydrocarbons, with nitro-sulphuric acid alone, substantially as hereinbefore described.

20. Products of the oxidation of paraffinic hydrocarbons whenever produced by the process of any preceding claim.

Dated this 27th day of June, 1949.

EDWARD EVANS & CO.,
14-18, High Holborn,
London, W.C.1,
Agents for the Applicants.

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