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OXIDATION OF ORGANIC COMPOUNDS

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The present invention relates to the oxidation of organic compounds.

It is already known that aliphatic i. e. open chain and cyclo-aliphatic hydrocarbons of high molecular weight, such as paraffin wax and paraffin oil, waxes such as Montan wax and like aliphatic open chain or cycloaliphatic bodies of high molecular weight or aliphatic alcohols and ketones of high molecular weight and mixtures containing the said compounds can be oxidized in the liquid phase with gases containing oxygen, such as air, oxygen, air enriched in oxygen or mixed with nitrogen oxides in the presence of different catalysts. Hitherto, single heavy metal compounds and single salts of the alkaline earth metals or of aluminium or of magnesium or mixtures of these salts (according to British Specification No. 310,069) and single metal enolates or mixtures thereof (according to the British Specification No. 303,268) have been proposed for this purpose. The temperatures of the oxidation are usually between 100° and 200° C., preferably between about 130° and about 170° C.

We have now found that the oxidation of aliphatic compounds of high molecular weight in the liquid phase can be carried out particularly rapidly by employing from a few per thousand, such as 0.5 per cent, up to 3 per cent, by weight of the initial materials of catalytic materials, which comprise one or more compounds of the alkali or alkaline earth metals including magnesium and aluminium on the one hand and of one or more compounds of the earth metals and/or heavy base metals on the other hand, which are converted into salts of the fatty acids formed during the oxidation and/or of mixtures of salts of organic acids with the metals of the said two groups. For the sake of brevity these compounds will be defined in the following and in the claims as being capable of dissolution in the reaction mass. Suitable catalysts are for example carboxylic acid salts especially those of higher acids, such as oleates, naphthenates, palmitates, cinnamates, abietates or other resinates, or mixtures thereof, which are soluble in the materials to be oxidized, and oxides, hydroxides, carbonates, as well as metal carbonyls and carbides, capable of being decomposed with water, which compounds become soluble in the oxidation products formed. Compounds of the crude acid oxidation products or of the acids contained therein with the said metals may also be employed. The compounds are preferably selected from the fatty acid salts, such as palmitates and oleates, or from

oxides, hydroxides or carbonates of the said metals.

The compounds of one group may be chosen from those of lithium, sodium, potassium, rubidium, cesium, calcium, barium, strontium, magnesium or aluminium, whereas those of the other group may be chosen from those of copper, zinc, cadmium, mercury, titanium, zirconium, cerium, thorium, tin, lead, vanadium, antimony, bismuth, chromium, molybdenum, tungsten, uranium, manganese, iron, cobalt or nickel, the rare heavy base metals such as niobium or thallium being applicable but out of consideration owing to their cost.

Suitable mixtures of the said compounds of heavy base metals are for example mixtures of compounds of Li+Ce, Na+Hg, Ca+Hg, Ca+Ce or Ba+Hg, and especially those of the 4th to the 8th groups of the periodic system with alkali metal or alkaline earth metal compounds including those of magnesium and aluminium, as for example mixtures of compounds of the metals, as for example of Na+V, Na+Cr, Na+Mn, Na+Fe, Mg+V, Mg+Cr, Ca+V, Ca+Cr, Ca+Mn, Ba+V, Ba+Cr, Ba+Fe, Al+V, Al+Mn, K+Mn, K+Al+Mn, Na+Al+V or of Mg with the said heavy base metals, which mixtures are especially active as catalysts. Combinations of several compounds of the heavy metals, as for example mixtures of the compounds of chromium and of vanadium with each other and additions of one or more compounds of the alkali or alkaline earth metals or of magnesium or aluminium besides those referred to also have a favourable action. These catalysts exhibit their favourable action even after the addition of very small amounts such as from 0.4 to 1 per cent by weight of the substances to be oxidized. Quantities substantially above 3 per cent do not show any particular increase of efficiency above those up to about 3 per cent. The catalysts may be added to the substance to be oxidized before the oxidation in one batch or may be added in small portions during the course of the oxidation. The ratio of the compounds of the said two groups may be varied in wide limits but the content of the mixtures of one component should be generally not below 10 per cent. The ratio depends largely on the molecular size of the compound employed, salts of the bases with long chain fatty acids being usually employed in higher quantities than salts with the lowest members of the fatty acid series or oxides or hydroxides of the bases. Thus, for example, the following

mixtures have proved very suitable for the purposes according to the present invention:

	Per cent of the mixture			
5	Ceric palmitate.....	20-30	preferably up to	65
	Calcium palmitate....	80-20	do do do	35
	Sodium palmitate....	5-75	do do do	37
	Vanadium palmitate..	95-25	do do do	63
	Aluminium palmitate	10-80	do do do	65
10	Vanadium palmitate..	90-20	do do do	35

Contrasted with the catalysts hitherto used, only about half the period of time is necessary in most cases in order to obtain the same degree of oxidation according to this invention, especially when employing catalysts which are soluble in the initial materials or in the products formed. Likewise an increased yield of oxidation products which usually consist of free acids, esters, alcohols, aldehydes, ketones and the like is obtained. When the oxidation is rendered incomplete by prematurely interrupting it, for example as soon as from 40, 50 or 75 per cent of the initial materials is still unattacked by the oxidation, and the unattacked initial material is separated, especially in the oxidation of hydrocarbons, high quality, particularly pale products are rapidly obtained by the employment of the catalysts according to this invention.

The superior action of the catalysts according to the present invention may be seen from the following comparative table in which the initial material in each case is a Pennsylvanian middle oil boiling from 180° to 350° C. and having a specific gravity of 0.8527 at 20° C. and an iodine value of 10.

	Catalyst	Duration of oxidation	Yield of oxidation product	Saponification value	Colour	
40	1 percent of nickel borate.....	8 hours..	90 per cent by weight of the initial material.	25	Dark brown.	40
	1 per cent manganese borate.....	8 hours..	89 per cent by weight of the initial material.	81	Do.	
45	1 per cent manganese borate and 0.2% calcium oxide.....	8 hours..	87 per cent by weight of the initial material.	116	Brown.	45
	1 per cent manganese palmitate.....	8 hours..	88 per cent by weight of the initial material.	110	Do.	
	1 per cent nickel palmitate.....	8 hours..	90 per cent by weight of the initial material.	88	Do.	
	1 per cent copper palmitate.....	8 hours..	92 per cent by weight of the initial material.	14	Do.	
50	0.6 per cent manganese palmitate and 0.4 per cent sodium palmitate.	4 hours..	101 per cent by weight of the initial material.	115	Dark yellow to pale brown.	50
	0.6 per cent manganese palmitate and 0.4 per cent calcium palmitate.	4 hours..	99 per cent by weight of the initial material.	109	Do.	
	0.6 per cent nickel palmitate and 0.4 per cent sodium palmitate.	4 hours..	102 per cent by weight of the initial material.	93	Do.	
55	0.6 per cent copper palmitate and 0.4 per cent sodium palmitate.	4 hours..	99 per cent by weight of the initial material.	36	Do.	55

In each case the experiments were carried out under identical conditions as regards amount of initial material, speed of flow of the air (1 cubic metre of air per kilogram of oil and per hour), temperature (160° C.), inert fillers (Raschig rings) and reaction space.

The said catalysts may be employed generally for the liquid-phase oxidation of liquid and solid aliphatic compounds of high molecular weight i. e. containing at least 8 carbon atoms, or mixtures thereof, as for example hydrocarbons such as hard or soft paraffin wax, crude paraffin wax, ceresine, paraffin oil, heavy or middle oils, naphthene hydrocarbons, petroleum fractions, such as gas oil, and hydrocarbons obtained synthetically, such as the products obtained by the destructive hydrogenation or low temperature carbonization of coals, brown coals, tars, mineral oil fractions and the like. Waxes, as for example Mon-

tan wax and the like as well as vegetal, i. e. animal or vegetable, oils or fats, as for example wool fat, coconut, sesamum, rapeseed, cottonseed, linseed or castor oils, or residues from the purification of these materials, fractions of turpentine oil boiling above 300° C. and non-aromatic alcohols and ketones of high molecular weight as are often obtained in mixture as unsaponifiable by-products in the oxidation of hydrocarbon materials are suitable.

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

100 parts of a middle fraction having a boiling point range of 180° to 350° C. derived from Pennsylvanian crude oil are heated to 180° C. for a short time after an addition of 0.4 part of iron carbonyl. The mixture is then treated with moist air at 160° C. in a cylindrical vessel filled with rings after the further addition of 0.6 part of pure calcium carbide, the speed of flow of the air being 1 cubic metre per hour per kilogram of initial material. After 5 hours a brown oxidation product is obtained the saponification value of which is 110.

Example 2

100 parts of Montan wax bleached with chromic acid and having the saponification value 120 are treated with air at 170° C. in a cylindrical vessel filled with rings after the addition of 0.6 part of vanadium palmitate and 0.4 part of calcium oxide, the speed of flow of the air being 1.5 cubic metres per hour per kilogram of ini-

tial material. After 8 hours a yellow product resembling bees wax to some degree and having a saponification value of 280 is obtained.

Example 3

100 parts of the mixture of neutral oxygen-containing compounds with hydrocarbons obtained after separating the acids by saponification with the aid of aqueous caustic soda at 100° C. and drawing off the oxygenated compounds from the soap solution, from an oxidation product of paraffin wax, prepared by blowing with air at 150° C. at the rate of 0.5 cubic metre per kilogram of wax in a tower filled with Raschig rings, are treated with dry air for 4 hours in a cylindrical vessel, containing rings as filling bodies, after the addition of 0.5 part of vanadium palmitate, 0.2 part of silver palmitate, and 0.3 part of sodium hydroxide, the speed of flow of the air

being 0.5 cubic metre per hour per kilogram of the initial material. A bright yellow oxidation product is obtained having a saponification value of 180.

Example 4

100 parts of a turpentine oil fraction boiling above 300° C. and having a saponification value of 28.3 are mixed with 0.15 part of aluminium palmitate, 0.10 part of vanadium palmitate and 0.05 part of sodium palmitate whereupon the whole is blown with air in a cylindric, vertical vessel at 165° C. in such a manner that 1 cubic metre of air is introduced at the bottom of the vessel through a sintered quartz plate per hour and per kilogram of the oil. After 5 hours a product is obtained which shows a saponification value of 105. If coconut oil or wool fat be worked in the same manner, the saponification values are increased from 258 to 325 and from 103 to 189 respectively by the formation of carboxylic acids.

What we claim is:—

1. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating, the step which comprises carrying out the reaction in the presence of up to about 3 percent, by weight of said compounds, of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and base heavy metals, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

2. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating, the step which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and the base heavy metals of the 4th to the 8th groups of the periodic system, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

3. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating to from 100° to 200° C., the step which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and base heavy metals, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

4. In the liquid-phase oxidation of aliphatic

compounds of high molecular weight by blowing the said compounds with air while heating to from 100° to 200° C., the step which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and base heavy metals, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

5. In the liquid-phase oxidation of paraffin by blowing with air while heating to from 130° to 170° C., the step which comprises carrying out the reaction in the presence of up to about 3 to 20 per cent, by weight of said paraffin, of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and base heavy metals, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

6. In the liquid-phase oxidation of a paraffin bearing mineral oil fraction by blowing with air while heating to from 130° to 170° C., the step which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said mineral oil fraction of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and base heavy metals, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

7. In the liquid-phase oxidation of a middle oil fraction of a mineral oil while heating to about 160° C., the step which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said middle oil fraction of a catalytic material consisting essentially of at least one compound of a metal selected from the group consisting of alkali-forming metals and aluminium, and at least one compound of a metal selected from the group consisting of earth metals except aluminium and base heavy metals, the said metal compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and carbonyls and carbides thereof, capable of being decomposed with water.

8. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating to from 100° to 200° C., the step which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consisting essentially of at least one carboxylate of a metal selected from the group con-

sisting of alkali-forming metals and aluminium, and at least one carboxylate of a metal selected from the group consisting of earth metals except aluminium and base heavy metals.

5 9. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating to from 100° to 200° C., the step
10 which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consist-
ing essentially of at least one carboxylate of an
alkali metal and at least one carboxylate of a
metal selected from the group consisting of earth
15 metals except aluminium and base heavy metals.

10. In the liquid phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating to from 100° to 200° C., the step
20 which comprises carrying out the reaction in the presence of up to about 3 per cent, by weight of said aliphatic compounds, of a catalytic ma-
terial consisting essentially of an aluminium car-
boxylate, at least one carboxylate of an alkali
25 metal and at least one carboxylate of a metal selected from the group consisting of earth metals except aluminium and base heavy metals.

11. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing
30 the said compounds with gases containing oxygen while heating, the step which comprises carry-
ing out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a
35 catalytic material consisting essentially of at least one salt of a fatty acid of a metal selected from the group consisting of alkali-forming met-
als and aluminium and at least one salt of a fatty acid of a metal selected from the group consist-

ing of earth metals except aluminium and base heavy metals.

12. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxy- 5
gen while heating, the step which comprises carry-
ing out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consisting essentially of
10 at least one salt of palmitic acid of a metal selected from the group consisting of alkali-form-
ing metals and aluminium and at least one salt of palmitic acid of a metal selected from the group consisting of earth metals except alumin-
ium and base heavy metals. 15

13. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating, the step which comprises
20 carrying out the reaction in the presence of up to about 3 per cent, by weight of the said compounds, of a catalytic material consisting essen-
tially of at least one compound of manganese and at least one compound of sodium, the said metal
25 compounds being selected from the group consisting of the carboxylic acid salts, oxides, hydroxides and carbonates of the said metals and
carbonyls and carbides thereof, capable of being decomposed with water.

14. In the liquid-phase oxidation of aliphatic compounds of high molecular weight by blowing the said compounds with gases containing oxygen while heating, the step which comprises
30 carrying out the reaction in the presence of up to about 3 per cent, by weight of said compounds, of a catalytic material consisting essentially of
35 manganese palmitate and sodium palmitate.

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