

### **Process for preparing alkyl hydroperoxide compounds**

5 The present invention relates to a process for manufacturing alkyl hydroperoxide compounds, more particularly the preparation of cyclohexyl hydroperoxide.

10 The invention relates more particularly to the preparation of cyclohexyl hydroperoxide by oxidation with oxygen of cyclohexane in a multistage reactor or reactors mounted in series.

15 Cyclohexyl hydroperoxide is an intermediate product obtained in the synthesis of adipic acid by oxidation of cyclohexane with oxygen.

20 Thus, in an industrially exploited process, liquid cyclohexane is oxidized by reaction with oxygen gas in a multistage reactor, at high temperature, to cyclohexane hydroperoxide. After separating out the unreacted cyclohexane, the hydroperoxide is decomposed into cyclohexanol and cyclohexanone, in the presence of a catalyst. The cyclohexanol/cyclohexanone mixture, 25 generally known as "olone", is then oxidized to adipic acid and other diacids with nitric acid. The adipic acid is extracted and purified, advantageously by crystallization.

30 In this process, it is important to obtain the highest possible yield of cyclohexyl hydroperoxide. This yield depends on the reaction implementation conditions, for instance the temperature and the oxygen concentration.

35 However, in order to avoid degrading this yield, it is necessary to avoid the decomposition of the cyclohexyl hydroperoxide. Specifically, this compound may decompose rapidly if the medium contains metallic species with high catalytic activity. Such metallic

species may often originate from corrosion of the metallic surfaces of the reactor, internal components contained in the reactor and also apparatus or devices attached to the reactors, in which the reaction medium  
5 circulates.

To avoid and limit this phenomenon, a process for the pyrophosphatation of metallic surfaces has been proposed for many years, as described in patent US 3  
10 510 526. To obtain this pyrophosphatation, the reactor and its internal components are subjected to a treatment with a pyrophosphate before the start of the oxidation reaction. It is necessary to repeat this treatment periodically, which entails a drop in the  
15 operating capacity of the equipment and thus affects the economy of the process.

Moreover, as the operating conditions of the reactor are very harsh (high temperatures and pressure, presence of compounds with high oxidizing power (oxygen, peroxides)), protection of the metallic surfaces with usual protective materials used in chemical reactors cannot be implemented efficiently, pyrophosphatation being virtually the only solution  
25 currently used.

One of the aims of the present invention is to propose a solution for efficiently protecting metallic surfaces under the operating conditions of the reactor and that  
30 do not require frequent replacement or periodical stoppages of the equipment.

To this end, the invention proposes a process for preparing alkyl hydroperoxide compounds, more particularly cyclohexyl hydroperoxide, comprising the  
35 placing of a liquid hydrocarbon, more particularly cyclohexane, in a reactor at a high temperature and at a high pressure in contact with oxygen. According to

the invention, the surfaces of the reactor in contact with the medium containing the hydroperoxide comprise a protective coat made of a perfluoroalkoxy polymer, generally referred to as a "PFA polymer".

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According to another characteristic of the invention, the reactor may comprise internal components such as plates, stirrers, probes, etc. The surfaces of these components in contact with the medium containing the alkyl hydroperoxide are advantageously protected with a protective coat made of "PFA polymer". Similarly, the devices and equipment attached to the reactor, such as pumps, circulation pipes and cyclohexane flash distillation apparatus, may be advantageously protected with a coating in accordance with the invention, i.e. a PFA polymer coating. Similarly, to avoid decomposition of the alkyl hydroperoxide during a storage phase, the storage device is advantageously protected with a protective coat made of PFA polymer.

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A large number of fluoropolymers exist. PFA polymers are a particular family of fluoropolymers. One of the most widely known fluoropolymers is PTFE (poly-tetra-fluoroethylene), sold under the brand name Teflon®.

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PFA or perfluoroalkoxy polymers are different from PTFE polymers especially in their meltable nature, i.e. they can be melted and thus formed via the standard processes used with thermoplastic polymers such as injection moulding and extrusion. PTFE therefore cannot be formed easily in equipment, for example to cover the inner walls of reactors. In addition, PTFE has high porosity, which gives rise to phenomena of absorption and desorption of certain chemical products during reaction, such as alcohols, ketones and acids produced by the oxidation of the hydrocarbon. Thus, the use of PTFE presents a large number of drawbacks that are

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particularly inconvenient in the context of the process of the invention.

These polymers were invented by the company DuPont de  
5 Nemours and are especially sold under the trade name  
Teflon-PFA. Other companies market equivalent polymers,  
for instance the company Daikin under the trade name  
Neoflon-PFA, or Solvay under the name Hyflon-PFA, or  
alternatively the company Gore, and more generally  
10 thermally and chemically resistant PFA polymers.

PFA polymers may also comprise mineral or organic  
fillers to improve their mechanical properties.  
However, in the context of the invention, these fillers  
15 should not comprise metallic elements.

By way of example of PFA polymers that are suitable for  
use in the invention, mention may be made of the  
various grades sold by the company DuPont de Nemours  
20 under the trade name PFA Ruby Red® or by the company  
Gore under the trade name Fluoroshield®.

The protective coat made of PFA polymers may be  
prepared according to the usual methods of deposition  
25 of polymer onto a surface or by applying PFA plates or  
sheets onto the surface to be protected.

Advantageously, the protective PFA coat has a thickness  
of between 500  $\mu\text{m}$  and 1 mm.

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Thus, by way of illustration, a polymer deposition  
process that may be mentioned is the electrostatic  
powder coating technique, which consists in applying  
several coats of polymers and in placing the protected  
35 apparatus in an oven to soften or melt the plastic  
grains so as to obtain a continuous film. This  
application process comprises a step of preparing the  
surfaces to be coated so as to free them of grease,

clean them and remove surface defects especially at the welds. An example that may be mentioned is the sandblasting process for obtaining a suitable surface state whose quality is indicated by the SA degree  
5 defined in standard SIS 05 59 00. After this cleaning, an anchoring priming coat is advantageously applied to the surface. This priming coat may advantageously comprise a PFA polymer. The protective coating is then produced by depositing one or more successive coats of  
10 PFA polymers, advantageously by electrostatic spraying of a PFA powder optionally suspended in a liquid.

Other techniques for producing the coating may be used, such as the technique proposed by the company Gore.  
15 Thus, in the system marketed by this company under the trade name Fluoroshield®, the process consists in attaching, for example by welding, a grille made of a material such as Inconel® onto the support to be protected and in applying a coat of PFA polymer onto  
20 this grille. Thus, the anchoring of the PFA polymer protection is reinforced.

In addition, this protection is advantageously used to protect metal surfaces, especially surfaces made of  
25 stainless steel, but it may be used to protect any type of metallic or non-metallic surface.

In one embodiment of the invention for the preparation of an alkyl hydroperoxide described as an example, the  
30 process consists in introducing the hydrocarbon such as cyclohexane into the bottom of a tubular reactor, simultaneously with the introduction of oxygen or a gas containing oxygen continuously. However, the invention also applies to processes using other types of reactor,  
35 especially with staged introduction of oxygen or introduction of the hydrocarbon into the top of the reactor.

The reaction pressure is between 10 and 30 bar, and the temperature is between 130°C and 200°C. The oxygen is introduced continuously into the headspace of the reactor at a flow rate of between 10 and 30 Nl/h. For safety reasons, the reaction conditions, especially the residence time in the reactor, are controlled so as advantageously to obtain in the reactor headspace a gas phase containing oxygen at a concentration lower than a critical value, of about 5% by volume, to limit the risks of auto-explosion and auto-ignition with hydrocarbon vapours. However, this characteristic is not obligatory.

The process of the invention makes it possible to limit the decomposition of hydroperoxide formed by the oxidation reaction and thus to improve the reaction yield, by limiting the contact between the reaction medium and the metallic surfaces.

According to the invention, it is also possible to perform a pyrophosphatation on the protective PFA polymer coat.

In addition, the protective PFA polymer coat has a very long service life and can thus improve the economy of the process by reducing the frequency of the stoppages necessary to renew or repair the protection.

Moreover, the protective PFA polymer coat has the advantage of not absorbing or releasing the chemical compounds produced during reaction such as cyclohexanol, cyclohexanone and by-products formed during the reaction, for instance acids, which limits the stoppages for cleaning the reactor.

It also constitutes an efficient barrier to interaction between the metallic walls and the reaction medium,

which can limit the decomposition of the hydroperoxide and thus improve the reaction yield.

Furthermore, the protective PFA polymer coat makes it possible to work at high temperature and has better creep resistance, i.e. deformation under a permanent stress. By way of example, under a load of 8.8 MPa (megapascals) at 150°C for 100 hours, and after 24 hours of relaxation, PFA has a remanent degree of deformation of 10%, whereas this is 34% for PTFE (test performed according to standard ASTM D621).

Other advantages and details of the invention will emerge even more clearly in the light of the examples given below for illustrative purposes.

#### EXAMPLES

Cyclohexane is placed in a reactor equipped with a self-priming turbomixer and a condenser. The stainless-steel reactor is either unclad, or pyrophosphate-clad or clad with a PFA coat. The reaction medium is heated to 165°C. When the temperature is reached, oxygen at 43% by volume in nitrogen is injected in at a flow rate of 30 Nl/h at a pressure of 30 bar. Samples are taken and analysed by gas chromatography to monitor the formation of cyclohexyl peroxide over time. No difference in selectivity towards HPOCH as a function of the degree of conversion is observed between a pyrophosphate-clad reactor and a reactor clad with a PFA coat; on the other hand, there is a great difference when compared with an unclad reactor.

#### - Reactor pyrophosphatation protocol:

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An aqueous sodium pyrophosphate solution at 5% by mass is introduced into the stainless-steel reactor. After stirring for 45 minutes at room temperature, the

reactor is emptied and then left to dry overnight at room temperature.

5     - Protocol for producing a PFA coating in accordance with the invention on the inner surface of reactor c:

Preparation of the support:

10     The surface to be coated undergoes the usual grease-removal, cleaning and sandblasting treatments. The surface defects and welds are flattened. This treatment may be localized or general to the entire component. The final surface state of the components to be coated is measured and qualified by the SA index defined in  
15     standard SIS 05 59 00. This index is 2.5.

Application of the coating:

20     Application is performed by spraying a PFA powder sold by the company DuPont as a suspension in water. This application comprises the electrostatic spraying of an anchoring priming coat based on PFA polymer. The reactor is heated to a temperature in the region of 400°C to allow baking of the priming coat. The baking  
25     temperature is generally supplied by the manufacturer of the PFA polymer sold by the company DuPont under the trade name Ruby Red® and depends on the nature of this polymer. A first PFA polymer coat is then applied over the priming coat according to the same technique, and  
30     the reactor is then brought to 400°C again to bake this coat. This operation is repeated as many times as necessary to obtain the desired thickness of the protective coat. For example, depending on the system, electrostatic powder coating is used. The quality and  
35     thickness of the protective coat are controlled, especially the homogeneity and the adhesion of the protective coat.

Tests for the production of cyclohexyl hydroperoxide were performed in an unprotected reactor, a pyrophosphatation-protected reactor and a reactor protected in accordance with the invention with a PFA coating, with identical operating conditions described above.

The mole percentage of cyclohexyl hydroperoxide (HPOCH) produced was measured for different degrees of conversion of cyclohexane. The results obtained are collated in Figure 1, which represents the variation in the molar amount of HPOCH produced as a function of the degree of conversion of cyclohexane for the three reactors used:

- Curve A: test in an unprotected stainless-steel reactor
- Curve B: test in a pyrophosphatation-protected stainless-steel reactor
- Curve C: test in a stainless-steel reactor protected with a PFA coating in accordance with the invention.

These results show that the coating in accordance with the invention affords protection equivalent to that obtained with the pyrophosphatation process.

### Claims

1. Process for preparing an alkyl hydroperoxide, comprising the placing of a liquid hydrocarbon in a reactor at a high temperature in contact with oxygen, characterized in that the surfaces of the reactor in contact with the medium containing the hydroperoxide comprise a protective coat made of a perfluoroalkoxy (PFA) polymer.
2. Process according to Claim 1, characterized in that internal components are arranged in the reactor, and the surface of the said components in contact with the medium containing the alkyl hydroperoxide comprises a protective coat made of a perfluoroalkoxy (PFA) polymer.
3. Process according to Claim 1 or 2, characterized in that the protective coat has a thickness of between 500  $\mu\text{m}$  and 1 mm.
4. Process according to Claims 1 to 3, characterized in that the protective coat is obtained by depositing PFA polymer.
5. Process according to Claims 1 to 3, characterized in that the protective coat is formed by a PFA film applied onto the surfaces to be protected.
6. Process according to one of Claims 1 to 3, characterized in that the protective coat is produced by arrangement and juxtaposition of PFA plates on the surfaces to be protected.
7. Process according to one of the preceding claims, characterized in that the alkyl hydroperoxide is cyclohexyl hydroperoxide, the hydrocarbon being cyclohexane.