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(54) **PROCESS FOR OBTAINING HIGH-OCTANE GASOLINE COMPONENTS AND A CATALYST**

(57) A process for preparing high-octane gasoline components consists in that a feed stock, composed of isobutane and olefins, preferably butylenes, in a molar ratio between 1 and 40, is contacted at temperatures of from about 50 to about 160°C and at pressures of from about 1 to about 40 atm. with a heterogeneous acid catalyst, whose active component is a metal-complex or metaloxopolymeric compound of the general formula  $H_k(Me^1)_l(Me^2)_mO_nX_p$ , wherein  $k = 1-6$ ;  $l = 1-3$ ;  $m = 1-5$ ;  $n = 1-10$ ,  $p = 2-10$ , dispersed in a porous organic or inorganic matrix, followed by the extraction regeneration of the deactivated catalyst with an organic or inorganic solvent.

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## Description

Technical field

5 The present invention relates to catalytic chemistry, more particularly, to processes for preparing high-octane gasoline components in the oil refining and petrochemical industries.

The present invention relates to an alkylation process which is based on reaction of isoparaffins with olefins to form isoparaffin hydrocarbons having a higher molecular weight.

10 Prior art

Alkylation of isobutane with butylenes is traditionally used in industry to form a mixture of isoparaffin hydrocarbons, a so-called alkylate with an octane number of from 82 to 92 MM. Typical catalysts of industrial alkylation processes are sulfuric acid or fluorinated derivatives thereof (EP 0 433 954 A1) and hydrofluoric acid. Artificial cold is used a process  
15 involving sulfuric acid to maintain low reaction temperatures at 3 to 8°C, at acid concentrations from about 88 to about 94% by weight by continuously adding a fresh acid to the reaction system and removing the spent one.

Hydrofluoric and sulfuric acid alkylation plants are being used in the world. However, hydrofluoric acid is more dangerous than sulfuric acid, that is why some countries refuse the construction of plants using this catalyst. A choice  
20 between these processes depends on an amount of operating costs and/or safety in operations.

A hydrofluoric acid alkylation process usually uses 0.5 to 0.8 kg of acid per ton of alkylate, whereas a sulfuric acid alkylation process uses a much greater amount of acid, namely 60 - 100 kg per ton of alkylate.

High acid consumption necessitates the use of acid regeneration plants which should be used in combination with an alkylation plant.

25 The world annual production of alkylate amounts to 51 mln. tons and is expected to grow by 5 times before the year of 2000 due to more rigid ecological norms for motor gasoline with respect to the content of tetraethyl lead, benzene and a total amount of aromatic hydrocarbons.

The widely known industrial alkylation technologies are disadvantageous in:

- high toxicity and corrosive aggression of sulfuric and hydrofluoric acids,
- 30 - problems of utilization of the spent acide,
- necessity for recovering a catalyst from a product mixture and subsequently making it alkaline, these factors cause a high ecological danger and insufficient economic efficiency from the industrial point of view.

In solving these problems, the last decade has witnessed intensive investigations on developing solid acid catalysts and carrying out an alkylating process in a gas (raw material) - solid (catalyst) or liquid (raw material)-solid (catalyst)  
35 heterogeneous system. This makes the process ecologically safer.

It is advisable to single out several approaches to the development of solid alkylation catalysts.

The first approach suggests improving an alkylation catalyst by applying (heterogenizing) an (traditional) active component that has been known for a long time to inorganic supports. The peculiar feature of this approach is using,  
40 as an active components, both proton-containing acids ( $H_2SO_4$ ; HF;  $CF_3SO_3H$ ) and Lewis acids ( $AlCl_3$ ,  $BF_3$ ,  $BCl_3$ ,  $SbF_5$ , and the like). The nature of patented is much more variegated. Two large groups of supports may be singled out.

1. Non-zeolite ones represented by oxides or a mixture of Group III or IV metal oxides modified with the additives of elements of from Groups I to VIII, more often than not with the oxides of rare-earth elements.

45 2. Wide-pore zeolites of X, Y, ZSM, or Beta, etc. types. This approach is illustrated by a number of the patented catalytic systems and processes based thereon.

In US Patent No. 2,804,491 the catalyst is represented by an aluming gel stabilized with silica and containing boron trifluoride. Solid inorganic Group IV metal oxides modified with sulfuric acid, represent the subjects of the inventions in  
50 Japanese Patents No. 51-63386; No. 57-3650; No. 59-40056, No. 59-6181 and also in US Patents No. 3.251.902; No.3.655.813; No. 4.377.721 for a process for alkylating isoparaffin hydrocarbons with olefins.

Sulfuric or fluorosulfonic acid applied to an inorganic support is claimed as alkylation catalysts in EP No. 433 954 A1.

Both acids applied in the form of a liquid phase to an inorganic or an organic support belonging to classes formed  
55 by macroreticular polymers, zeolites, oxides of Groups III-VIII metals or a combination thereof are claimed as catalysts for the alkylation of isoparaffins with olefins in European Application No. 0 542 620 A1.

Lewis acids of  $AlCl_3$ ,  $BF_3$ ,  $BCl_3$ ,  $SbF_5$  types, applied to solid non-zeolite inorganic oxides (US Patent No. 4.956.518) and zeolites of ZSM-4, ZSM-18, ZSM-20 types, Beta zeolite (US Patent No 4.992.616; 4.384.161, PCT/US/92/00948) the alkylation of isobutane was catalyzed with butylenes.

The application of wide-pore zeolites in combination with Lewis acids enhanced, according to the patent, catalyst activity and alkylation selectivity. A disadvantage of catalysts of this type is employment of high-toxic and aggressive compounds as the active catalyst component.

The second approach resides in searching and synthesizing an active component of a new nature from a class of solid acids. First of all, it is necessary to intensify the acid properties of different zeolites by varying the cationic form and to use a dealuminizing process.

This approach is illustrated by wide-pore crystalline aluminosilicates -- zeolites X, Y and cationic forms thereof, which are recommended as alkylation catalysts in US Patents No. 100 3.251.902, No.3.549.557, No.3.655.813, No. 3.893.942, No. 4.992.615; in French Patent No.1.598.716 and in German Patent No. 118.181, in USSR inventor's Certificate No. 1622358.

The third approach is based on the use of a polymeric matrix with grafted (immobilized) functional groups displaying strong acid properties.

Macroreticular organic ion-exchange resins in the cationic form are disclosed as alkylation catalysts in US patents No. 3.862.258; No. 3.855.342.

The analysis set forth above deals with new processes of alkylation of isoparaffin hydrocarbons (isobutane above all) with olefins (butylenes) for producing a high-octane gasoline component (a mixture of isoparaffin hydrocarbons), for which purpose solid acid catalysts of a different nature are used.

However, these catalysts have low power expressed in an amount of alkylate obtained from one gram of catalyst in a run between two regenerations and also show low alkylate efficiency expressed in grams of alkylate per gram of catalyst for an hour. Most patents provide experimental data obtained in a periodic mode in an autoclave. For the reasons, scaled above, these said catalysts have not thus far found their practical application and have not been introduced on an industrial scale.

Known is a process for alkylating isoparaffins containing 4 to 22 carbon atoms with olefin containing 2 to 12 carbon atoms (US Patent No. 4.992.616), characterized in that the catalyst employed is represented by wide-pore ZSM-3, ZSM-4, ZSM-12, ZSM-18, ZSM-20, zeolites modified with Lewis acids ( $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{BCl}_3$ ,  $\text{SbF}_5$ ) in the presence of water or compounds containing it to improve process performance. As a result of use of a new catalyst the productivity of a reactor volume, the yield of the initial olefin and power are as follows:

2.0 - 2.1  $\text{g/g}_{\text{catalyst}} \times \text{hr}$   
 190-210 % by weight  
 500-600  $\text{g}_{\text{alkylate}}/\text{g}_{\text{catalyst}}$

The claimed process is disadvantageous in that a catalyst containing high-toxic corrosion-active Lewis acids is used and that it cannot be regenerated.

Disclosed in Japanese Patent No. 61-242461 (A) is a catalyst for alkylating isoparaffins with olefins, which catalyst is obtained by introducing a sulphuric acid component and rare earth element compounds into the Group IV, metal oxide followed by activation through calcination at temperature comprised between 400 and 800°C. The alkylation process is conducted at temperatures from 0 to 200°C, a pressure between 1 and 60 atm., a feed stock containing isobutane and olefins with a molar ratio of 1 to 20, respectively. As a result of application of a new catalyst the productivity of a reactor volume, the initial olefin yield and the catalyst power are as follows:

0.2 - 0.3  $\text{g/g}_{\text{catalyst}} \times \text{hr}$   
 99 - 100 % by weight  
 20- 50  $\text{g}_{\text{alkylate}}/\text{g}_{\text{catalyst}}$

The deactivated catalyst may be subjected to oxidizing regeneration by calcination in the air at a temperature comprised between 400 and 500°C.

A disadvantage of the claimed catalyst is low power and a low alkylate yield per initial olefin.

## Description of the invention

It is the principal object of the present invention to provide an ecologically safe process for preparing high-octane gasoline components on a heterogeneous solid acid catalyst by alkylating isobutane with butylenes.

Said object is attained by charging into a reactor vessel a catalyst which comprises

- an active component in the form of a metal-complex or metaloxopolymeric compound of the general formula  $\text{H}_k(\text{Me}^1)_l(\text{Me}^2)_m\text{O}_n\text{X}_p$ , wherein  $k = 1 - 6$ ;  $l = 1 - 3$ ;  $m = 1 - 5$ ;  $n = 1 - 10$ ,  $p = 2 - 10$ , which is chemically fixed or applied to the surface of an inorganic matrix, wherein  $\text{Me}^1$  - a metal, Group IV; Ti, Zr, Hf, Sn;  $\text{Me}^2$  - a metal, Groups II -IV;  $\text{X} = \text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{FSO}_3^-$ ,  $\text{ClSO}_3^-$ ,  $\text{FPO}_2^-$ ,  $\text{F}_2\text{PO}_2^-$ , or any combination thereof, the active component being

dispersed on the surface of a porous matrix in the form of particles having a typical size of from about 10 to 500Å ;

- a matrix comprising a porous inorganic or organic material;
- the Groups II-IV metal oxide;
- the Group VIII metal such as Pt, Pd, Ru, Os, Ir.

5

The investigations of the inventors showed that isobutane alkylation with olefins proceeds most effectively on a catalyst comprising the metal-complex or metaloxopolymeric compound of the Group IV metal of said general formula, which catalyst is applied or chemically fixed on the surface of a porous inorganic or organic material, and along with this, the improved catalyst activity, as compared to the prior art catalyst activity is ensured by:

10

- a) a stoichiometric composition of an active acid catalyst component that determines a narrow range of active acid centers which selectively catalyze precisely the isobutane alkylation reaction;
- b) a high degree of dispersion of a metal-complex compound on the surface of a porous support, which leads to increasing the number of active centers participating in the reaction.

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Various porous inorganic materials have been used for preparing a catalyst: high-silica zeolites, the oxides of the Groups II - IV elements or mixtures thereof, porous carbon materials and polymers porous organic.

Increased catalyst activity and improved selectivity are achieved by introducing the oxides of the Groups II-IV elements into the catalyst composition, this occurs due to the increased activity of the catalyst surface in a hydrogen disproportionation reaction promoting a fuller involvement of an isobutane component of the feedstock into the alkylation process.

20

An increased catalyst power and improved selectivity with respect to the most high-octane components of alkylate such as trimethylpentanes, is likewise attained by introducing the Group VIII elements into the catalyst composition and by conducting a process of alkylation in hydrogen or a hydrogen-containing gas. In this case there occurs hydrogenation of high-molecular olefin hydrocarbons which deactivate the active catalyst surface.

25

The highest catalyst activity, selectivity and power are achieved when the alkylation process is conducted at temperatures and pressures ensuring the supercritical state of the feed stock components in the reactor volume.

It has been found that the introduction into the feed stock for alkylation of hydrocarbons having from 5 to 10 carbon atoms in an amount of from 10 to 20% by weight increases the catalyst power. A high dissolving power of hydrocarbons results in removing, from the reactor volume, olefin polymerization products which deactivate the catalyst, thus making the run between two regenerations longer and the catalyst power greater.

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The claimed composition relates to multi-action catalysts, i.e. it is capable of fully restoring its catalyst properties (activity, selectivity, power) after regeneration.

In the claimed alkylation process, a catalyst is regenerated by extracting the deactivating components from the catalyst surface using a solvent at elevated temperatures and pressures. To wash the catalyst bed, use can be made of single-component or complex solvents belonging to different classes of organic substances.

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Such solvents include:

- aromatic hydrocarbons: benzene, toluene, xylenes, etc.;
- oxygen-containing organic compounds - ether, dioxane, methyl-ethyl ketone, etc.;
- halogen-containing organic compounds: carbon tetrachloride, dichloromethane, dichloroethane, etc.;
- inorganic solvents: carbon dioxide, sulfur dioxide.

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The solvent is fed into a reactor space at a temperature comprised between 50 and 200°C and a pressure that allows for the solvent to be present in the reactor in the liquid state.

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A regeneration process results, in such conditions, in extracting resinous products from the active catalyst centers and in regenerating catalyst activity, selectivity and power similar to those of a fresh catalyst.

The regeneration of catalyst activity, using the devised method does not change, as distinct from traditional oxidizing regeneration at high temperatures, the morphological and structural characteristics of catalyst grain (surface, porosity), a factor that increases the catalyst service life by many times.

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The increase or decrease of the content of the corresponding components outside the said range results in reducing the target product yield due to a lower conversion of butylenes and a lower yield of alkylate per the initial butylene, and also to a lower catalyst power .

#### 55 Preferred embodiment of the invention

The process for preparing high-octane gasoline components of an isoparaffin nature is carried out in using, as the feed stock components, isobutane and butylenes of different isomeric compositions, or hydrocarbon fractions containing isobutane and butylenes. In the examples as given below catalyst activity, selectivity, productivity and power have

been obtained in using, as the alkylation feedstock industrial hydrocarbon fractions (wt.%):

Isobutane fraction		Butylene fraction	
C2	0.1	C2	0.1
C3	1.5	C3	7.8
butane	3.9	butane	17.0
isobutane	93.2	isobutane	37.7
butylenes	1.2	butylenes	34.1
C5+ hydrocarbons	0.4	C5+ hydrocarbons	3.3

An alkylation catalyst is prepared in the following manner: first synthesized is a metal-complex compound. A porous support is impregnated with an aqueous solution of said metal-complex compound and dried at a temperature comprised between 100 and 200°C. An active catalyst component is finally formed by calcination at a temperature of from about 400 to about 600°C in atmospheric air or inert gas.

To grasp a better idea of the concept of the present invention, the concrete examples are given below.

#### Example 1

20 g of a silica gel are mixed with 20 ml of an aqueous solution containing 2.34 g of zirconyl nitrate and 0.043 g Pt in the form of chloroplatinic acid. Dried at 110°C for 10 hours, thereafter calcined at 550°C for 3 hours to give an alkylation catalyst support.

In 100 ml of an aqueous solution containing 50 g of zirconylsulfuric acid are dissolved in 8.81 g of zinc chloride, with a metal-complex compound forming in the solution. The compound has the formula  $\text{HZnZrO}(\text{SO}_4)_2$ . The resulting solution is maintained on a water bath, at 95°C for 5 hours.

Into the resulting solution is introduced a support for an alkylation catalyst, maintained for 3 hours, dried at 150°C for 10 hours and calcined at 550°C for 3 hours. The alkylation catalyst obtained is of the following chemical composition:  $\text{ZrO}_2$  - 5.4% by weight,  $\text{HZnZrO}(\text{SO}_4)_2$  - 12.2% by weight,  $\text{SiO}_2$  - 81.0% by weight, Pt - 0.2% by weight.

A flow-through tubular reaction vessel is charged with a catalyst (10 g). The reaction vessel is preheated up to 75°C, blown out with helium, followed by an isobutane fraction passed at a rate of 3 g/g<sub>catalyst</sub> hr for 1 hour. After isobutane blowing, the feed stock is fed, the latter is prepared by mixing 0.37 kg of a butylene fraction and 1.00 kg of said isobutane fraction at a rate of 6.4 g/ml<sub>cat</sub>× hr. The molar ratio of isobutane to butylenes in the feed stock is 10.3. The pressure in the reaction vessel is 17 atm. Reaction products are admitted to a separator through a pressure regulator, said separator being cooled to 0°C. Gaseous and liquid products are assayed separately, using a chromatographic analysis. The process is conducted for 400 hours.

On the basis of chromatographic analysis data is calculated:

- productivity of the reactor volume (g<sub>alkylate</sub>/ml<sub>cat</sub> per hr) -  $P = M_a / V_{cat}$ , wherein  $M_a$  - the quantity of liquid alkylate in g, which is formed in a one hour reaction,  $V_{cat}$  - the catalyst volume, ml;
- conversion of butylenes (%) according to the formula:  $X = 100 \times (C_n - C_k) / C_n$ , wherein  $C_n$  - the concentration of butylenes at the reactor inlet mol %,  $C_k$  - the concentration of butylenes at the reactor outlet mol %;
- the yield of alkylate per initial olefin:  $A = P / (W \times C_n^v)$ , wherein P - the productivity of the reactor volume, W - the feed stock feed rate, expressed in g/ml<sub>cat</sub>× hr,  $C_n^v$  - the concentration of butylenes in the feed stock, % by weight;
- the content of trimethylpentanes in the alkylate:  $\text{TMP} = M_{\text{tmp}} / M_{\text{alkylate}} \times 100$ , wherein  $M_{\text{tmp}}$  - the amount of trimethylpentanes in the alkylate in g,  $M_{\text{alkylate}}$  - the amount of the alkylate resulting from the reaction, in g; TMP - the concentration of trimethylpentanes in the alkylate, % by weight;
- the catalyst power  $P = P \times T$ , wherein  $R_r$  the productivity of the reactor volume, T - the time during which olefin conversion is reduced by 10%.

The Process results:

the alkylate efficiency,  $E = 0.93$  g/ml<sub>cat</sub> per hr

the average butylene conversion (for 400 hours),  $X = 97\%$

the liquid alkylate yield per initial butylenes  $A = 202\%$

the catalyst power,  $P = 195 \text{ g/ml}_{\text{cat}}$ .

Example 2

5 Alkylate is prepared in the same manner as in Example I, with the exception that the isobutane/butylene feed stock is saturated with hydrogen under the pressure of 25 atm. The catalyst characteristics, the conditions and the process results are given in Table 1.

Examples 3-11

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Alkylate is prepared in the same manner as in Example I, with the exception that in addition to temperature, the feed stock rate, the pressure and the molar ratio of isobutane/butylenes are varied. The catalyst characteristics, the conditions and the process results are given in Table I.

15 Examples 12-22

Alkylate is prepared in the same manner as in Example I, with the exception that composition and the quantity of a metal-complex compound applied to the surface of a silica gel are varied. The catalyst characteristics and the process conditions are given in Table 2 and in Figures.

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Examples 23-32

Alkylate is prepared in the same manner as in Example I, with the exception that varied is the chemical nature of a porous support is varied. The characteristics and the process results are given in Table 3.

25

Examples 33-34

Alkylate is prepared in the same manner as in Example I, with the exception that the degree of dispersion of an active component in the catalyst is varied. The catalyst characteristics and the process results are given in Table 4 and in Figs. 1, 2.

30

Example 35

35 Alkylate is prepared in the same manner as in Example I, with the exception that the feed stock is added with an alkylate in an amount of 15.2% by weight. The process performance is as follows:

- the alkylate efficiency,  $E = 0.95 \text{ g/ml}_{\text{cat}} \cdot \text{x hr}$
- the average butylenes conversion (for 13 5 hrs),  $X = 97\%$
- the liquid alkylate yield per initial butylene  $A = 205\%$
- 40 the catalyst power,  $R = 249 \text{ g/ml}_{\text{cat}}$
- the content of trimethylpentanes,  $\text{TMP} = 76.3\%$

Example 36

45 The deactivated catalyst of Example I is treated in a tubular reactor in a toluene flow,  $5 \text{ g/g}_{\text{cat}} \cdot \text{x hr}$  at  $170^\circ\text{C}$ , pressure 15 atm., for 5 hours. The regenerated catalyst has the following characteristics:

- the alkylate efficiency,  $E = 0.95 \text{ g/ml}_{\text{cat}} \cdot \text{x hr}$
- the average butylenes conversion (for 400 hrs),  $X = 98\%$
- 50 the liquid alkylate yield per initial butylenes,  $A = 200\%$
- the catalyst power,  $P = 195 \text{ g/ml}_{\text{cat}}$ .

Example 37

55 The deactivated catalyst of Example I is treated in a tubular reactor in an ether flow,  $3 \text{ g/g}_{\text{cat}} \cdot \text{x hr}$ , at  $90^\circ\text{C}$ , the pressure 29 atm. for 5 hours. The regenerated catalyst has the following characteristics:

- the alkylate productivity,  $P = 0.85 \text{ g/ml}_{\text{cat}} \cdot \text{x hr}$
- the average butylenes conversion (for 400 hours),  $X = 96\%$

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liquid alkylate yield per initial butylenes  $A = 180\%$   
the catalyst power,  $R = 174 \text{ g/ml}_{\text{cat}}$ .

### Example 38

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The deactivated catalyst of Example I is treated in a tubular reaction vessel in a dichloroethane flow,  $7 \text{ g/g}_{\text{cat}} \times \text{hr}$ , at  $110^\circ\text{C}$  a pressure  $35 \text{ atm.}$ , for 5 hours. The regenerated catalyst has the following characteristics:

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the alkylate efficiency,  $E = 0.99 \text{ g/ml}_{\text{cat}} \times \text{hr}$ .  
the average butylenes conversion (for 400 hours),  $X = 98\%$   
the yield of liquid alkylate yield per initial butylenes,  $A = 195\%$   
the catalyst power,  $R = 192 \text{ g/ml}_{\text{cat}}$ .

### Example 39

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The deactivated catalyst of Example I is treated in a tubular reaction vessel in a carbon dioxide flow,  $9 \text{ g/g}_{\text{cat}} \times \text{hr}$ , at  $60^\circ\text{C}$ , a pressure  $90 \text{ atm}$ , for 5 hours. The regenerated catalyst has the following characteristics:

20

the alkylate efficiency,  $E = 0.97 \text{ g/ml}_{\text{cat}} \times \text{hr}$ .  
butylenes conversion (for 400 hours),  $X = 98\%$   
the liquid alkylate, yield per initial butylenes  $A = 204\%$   
the catalyst power,  $p = 197 \text{ g/ml}_{\text{cat}}$ .

### Industrial applicability

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The claimed process may find a variety of applications in the industry to obtain ecologically pure fuels. Can be utilized in various branches of the chemical industry, including the oil refining industry.

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TABLE 1. The influence of temperature, pressure, phase state and feed stock rate, isobutane /butylenes molar ratio on the alkylation process performance. The alkylation catalyst comprises:  $ZrO_2$ -5.4, % by weight,  $HfZrO(SO_4)_2$ - 12.2, % by weight,  $SiO_2$ -81.0, % by weight, Pt - 0.2, % by weight

N	T, °C	P, atm	feed stock crit. param.	Phase state	feed stock feed rate, g/ml. .hr	Iso-butylene, mol	P, g/ml.hr	X, %	A, %	Power g/ml	TMP % by weight
1	2	3	4	5	6	7	8	9	10	11	12
1	75	17	$T_{cr}=136^\circ C$	liquid	6.4	10.3	0.93	97	202	195	72.3
			$P_{cr}=36$ atm.								
2	75	17	$T_{cr}=136^\circ C$	liquid	6.4	10.3	0.93	97	202	390	72.3
			$P_{cr}=36$ atm								
3	160	39	$T_{cr}=136^\circ C$	super-critical	6.3	10.3	0.99	99	201	198	72.0
			$P_{cr}=36$ atm								
4	160	39	$T_{cr}=136^\circ C$	super-critical	5.1	5.8	0.94	95	169	169	71.4
			$P_{cr}=36$ atm								
5	160	12	$T_{cr}=136^\circ C$	gas	6.3	12.9	0.71	99	203	105	54.2
			$P_{cr}=36$ atm								



TABLE 1. (continued)

1	2	3	4	5	6	7	8	9	10	11	12
6	135	32	$T_{cr}=136^{\circ}\text{C}$	critical							
			$P_{cr}=36\text{ atm}$		8.1	12.9	0.90	99	199	195	59.8
7	100	15	$T_{cr}=136^{\circ}\text{C}$	gas							
			$P_{cr}=36\text{ atm}$	liquid	5.1	12.9	0.53	95	186	not found	56.1
8	100	8	$T_{cr}=136^{\circ}\text{C}$								
			$P_{cr}=36\text{ atm}$	gas	1.9	15.6	0.13	96	184	not found	42.4
9	100	8	$T_{cr}=136^{\circ}\text{C}$								
			$P_{cr}=36\text{ atm}$	gas	1.9	5	0.15	93	165	159	37.2
10	80	8	$T_{cr}=136^{\circ}\text{C}$	gas	1.0	12	0.07	86	132	not found	39.9
			$P_{cr}=36\text{ atm}$								
11	50	I	$T_{cr}=136^{\circ}\text{C}$								
			$P_{cr}=36\text{ atm}$	gas	1.0	12	0.08	69	144	100	48.4

TABLE 2. The influence of the composition and quantity of a metal-complex compound applied to a silica gel. Alkylation temperature 75°C, pressure 17 atm., feed stock feed rate speed 1.0 g/ml<sub>cat</sub> x hr. Isobutane/butylenes molar ratio = 5.8, feed stock feed rate - 4.2 g/g<sub>cat</sub>. x hr

N	Catalyst, chem. composition, % by weight	P g/ml	X hr	A %	Power g/ml	TMP % by weight
1	2	3	4	5	6	7
12	0.6 TiO <sub>2</sub> , 7.2 HZnTiO(SO <sub>4</sub> ) <sub>2</sub> , 92.2 SiO <sub>2</sub>	0.25	98	195	167	70.3
13	1.8 TiO <sub>2</sub> , 12.2 Zn <sub>2</sub> I TiO(SO <sub>4</sub> ) <sub>2</sub> , 86 SiO <sub>2</sub>	0.24	99	186	169	71.0
14	0.9 TiO <sub>2</sub> , 11.8 H <sub>2</sub> Al <sub>2</sub> TiO(SO <sub>4</sub> ) <sub>2</sub> , 0.5 Pt, 86.8 SiO <sub>2</sub>	0.21	94	199	184	73.4
15	10.2 H <sub>2</sub> TiF <sub>6</sub> , 5.0 SnO <sub>2</sub> , 84.4 SiO <sub>2</sub>	0.16	91	146	111	54.2
16	1.8 TiO <sub>2</sub> , 13.0 H <sub>3</sub> Al <sub>3</sub> Ti <sub>3</sub> T <sub>12</sub> , 0.2 Pt, 85.0 SiO <sub>2</sub>	0.18	95	151	153	59.8
17	1.8 TiO <sub>2</sub> , 10.2 HZnTiOF <sub>4</sub> , 88 SiO <sub>2</sub>	0.18	84	142	not found	56.1
18	0.5 ZrO <sub>2</sub> , 10.5 H <sub>2</sub> ZrO(SO <sub>4</sub> ) <sub>2</sub> , 0.5 Pt 88.5 SiO <sub>2</sub>	0.27	99	210	169	42.4

TABLE 2. (continued)

1	2	3	4	5	6	7
19	15.5 HZnZrO(SO <sub>4</sub> ) <sub>2</sub> , 20.6 ZrO 63.9 SiO <sub>2</sub>	0.23	97	183	174	49.1
20	2.0 ZrO <sub>2</sub> , 11.5 H <sub>6</sub> Al <sub>3</sub> Zr <sub>2</sub> O <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> , 0.1 Pt 86.4 SiO <sub>2</sub>	0.15	81	119	not found	39.9
21	2.0 ZrO <sub>2</sub> , 7.2 H <sub>2</sub> ZrO(ClSO <sub>4</sub> ) <sub>2</sub> , 90.8 SiO <sub>2</sub>	0.26	99	210	95	48.3
22	12.0 ZrO <sub>2</sub> , 27.0 H <sub>2</sub> AlZrO (FSO <sub>3</sub> ) <sub>2</sub> , 0.01 Pd 60.99 SiO <sub>2</sub>	0.26	99	210	118	59.9

TABLE 3

5 The influence of the nature of a porous alkylation catalyst support on the alkylation process performance. Alkylation temperature 100°C, pressure 8 atm, feed stock feed rate 4.3 g/ml<sub>cat</sub>. x hr. Isobutane/butylenes molar ratio = 8. The catalyst composition: ZrO<sub>2</sub>- 0.8% by weight; HAlZro (SO<sub>4</sub>)<sub>2</sub>, 12.2 % by weight, porous support 87.0%.

No	Porous support	P, g/ml x hr	X, %	A, %	R, g/ml
1	2	3	4	5	6
23	Gamma- Alumina	0.25	86	93	250
24	Carbon support "Sibunit"	0.55	97	189	192
25	Amorphous aluminosilicate	0.54	92	195	180
26	Copolymer of styrene and divinylbenzene	0.57	95	199	190
27	Zeoline ZSM-5, agglomerated crystals of foliaceous morphology, typical size 0.1 mcm, 94.5 SiO <sub>2</sub> , 3.53 Al <sub>2</sub> O <sub>3</sub> , 0.6 Fe <sub>2</sub> O <sub>3</sub> , 0.39 Na <sub>2</sub> O	0.23	97	183	174
28	Zeolite ZSM-5, agglomerated crystals of foliaceous morphology, typical size 0.7 mcm, 94.5 SiO <sub>2</sub> , 2.4 Al <sub>2</sub> O <sub>3</sub> , 0.9 Fe <sub>2</sub> O <sub>3</sub> , 0.01 Na <sub>2</sub> O	0.23	98	185	153
29	Zeolite ZSM-5, crystals of hexagonal morphology, typical size 3-4 mcm, 97.3 SiO <sub>2</sub> , 1.6 Al <sub>2</sub> O <sub>3</sub> , 0.9 Fe <sub>2</sub> O <sub>3</sub> , 0.04 Na <sub>2</sub> O	0.12	71	103	not found
30	Zeolite ZSM-12, agglomerated crystals of hexagonal morphology, typical size 98.5 SiO <sub>2</sub> , 1.4 Al <sub>2</sub> O <sub>3</sub> , 0.09 Fe <sub>2</sub> O <sub>3</sub> , 0.01 Na <sub>2</sub> O	0.21	95	174	109

TABLE 3 (continued)

The influence of the nature of a porous alkylation catalyst support on the alkylation process performance. Alkylation temperature 100°C, pressure 8 atm, feed stock feed rate 4.3 g/ml<sub>cat</sub> x hr. Isobutane/butylenes molar ratio = 8. The catalyst composition: ZrO<sub>2</sub>- 0.8% by weight; HAlZro (SO<sub>4</sub>)<sub>2</sub>, 12.2 % by weight, porous support 87.0%.

No	Porous support	P, g/ml x hr	X, %	A, %	R, g/ml
1	2	3	4	5	6
31	Zeolite Beta, agglomerated crystals, typical size 0.7 mcm 95.8 SiO <sub>2</sub> , 3.3 Al <sub>2</sub> O <sub>3</sub> , 0.03 Fe <sub>2</sub> O <sub>3</sub> , 0.03 Na <sub>2</sub> O	0.25	98	203	153
32	Zeolite Beta, agglomerated crystals, typical size 0.5 mcm, 92.7 SiO <sub>2</sub> , 7.1 Al <sub>2</sub> O <sub>3</sub> , 0.03 Fe <sub>2</sub> O <sub>3</sub> , 0.08 Na <sub>2</sub> O	0.24	98	192	120

TABLE 4

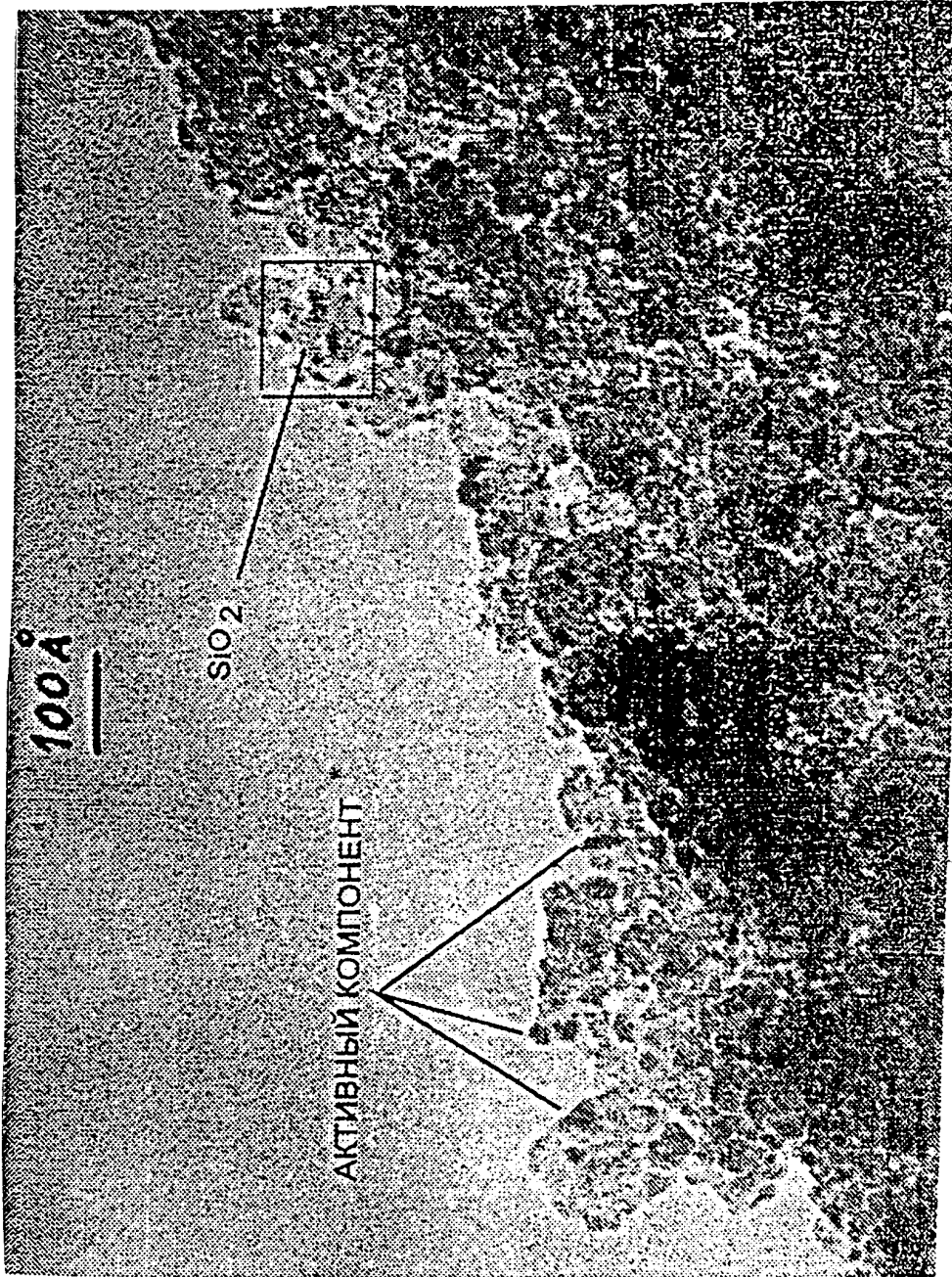
The influence of the degree of dispersion of an alkylation catalyst active component on the alkylation process performance. Alkylation temperature 100°C, pressure 23 atm, feed stock feed rate 4.3 g/ml<sub>cat</sub> x hr. Isobutane/butylenes molar ratio = 8. Catalyst composition: ZrO<sub>2</sub>- 0.8 % by weight, HAlZro(SO<sub>4</sub>)<sub>2</sub>, 11-12% by weight, porous support 87,0%

No	Porous support	Active comp. dispersion, A	P, g/ml · hr	X, %	A, %	R, g/ml
33	Silica gel	30-50 (Fig.1)	0.55	94	183	251
34	Carbon support "Sibunit"	30-100(Fig.2)	0.57	97	189	280

#### Claims

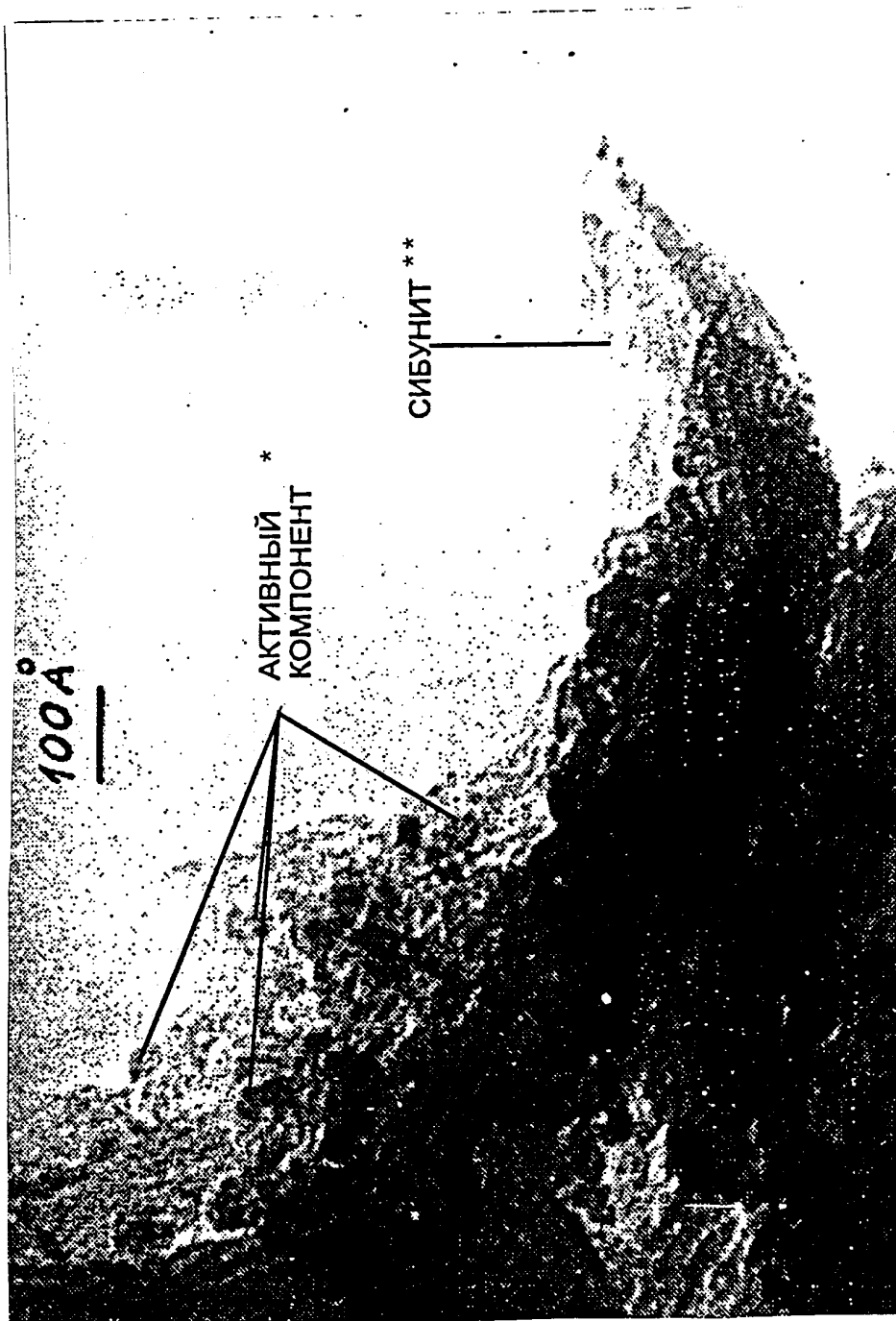
1. A process for preparing high-octane gasoline components by contacting feed stock composed of isobutane and olefins, preferably butylenes, with a heterogeneous acid catalyst at temperatures of from about 50 to about 160°C and pressures between 1 and 40 atm., with the isobutane/olefins ratio in a zone of alkylation maintained at 1 to 40, characterized in that for the process to be conducted, use is made of a solid heterogeneous acid catalyst containing a metal-complex or metalloxopolymeric compound of the general formula  $H_k(Me^1)l(Me^2)_mO_nX_p$ , wherein  $k=1-6$ ;  $l=1-3$ ;  $m=1-5$ ;  $n=1-10$ ,  $p=2-10$ , dispersed on the surface of a porous matrix in the form of particles having a typical size between 10 and 500 Å.
2. A process of claim 1, characterized in that alkylation is conducted at temperatures and pressures interrelated by the relationship  $P=F(T)$ , with which all the feed stock components are admitted to a reactor volume in the super-critical state.

3. A process of claim 1, characterized in that all the feed stock components are admitted to said reactor volume in the liquid state.
- 5 4. A process of claim 2 or claim 3, characterized in that said alkylation feed stock is further added with a hydrocarbon having from 5 to 10 carbon atoms in an amount between 1 and 20% by weight.
5. A process of claim 2 or claim 3, characterized in that said alkylation feed stock is further added with hydrogen or hydrogen-containing gas in an amount between 0.5 and 5% by weight.
- 10 6. A catalyst for preparing high-octane gasoline components by contacting a feed stock composed of isobutane and olefins at temperatures of from 50 to 160°C and pressures of from 1 to 40 atm., characterized in that it represents a metal-complex or metaloxopolymeric compound of the general formula  $H_k(Me^1)_l (Me^2)_m O_n X_p$ , wherein  $k=1-6$ ;  $l=1-3$ ;  $m=1-5$ ;  $n=1-10$ ,  $p=2-10$ , dispersed on the surface of a porous matrix in the form of particles having a typical size between 10 and 500 Å.
- 15 7. A catalyst of claim 6, characterized in that said metal-complex compound of the general formula  $H_k(Me^1)_l (Me^2)_m O_n X_p$  comprises IV metal, wherein  $Me^1 = Ti, Zr, Hf$ .
- 20 8. A catalyst of claim 6, characterized in that said metal-complex compound of the general formula  $H_k(Me^1)_l (Me^2)_m O_n X_p$  comprises Group II-III metal, wherein  $M^2 = Zn, Cd, Al$ .
9. A catalyst of claim 6, characterized in that said metal-complex compound of the general formula  $H_k(Me^1)_l (Me^2)_m O_n X_p$  comprises as a ligand, anions:  $X = F^-, Cl^-, SO_4^{2-}, PO_4^{3-}, FSO_3^-, ClSO_3^-, FPO_3^{2-}, F_2PO_2^-$ , or any combination thereof.
- 25 10. A catalyst of claim 6, characterized in that the catalyst comprises said metal-complex compound in an amount between 3 and 50% by weight.
11. A catalyst of claim 6, characterized in that the catalyst further comprises a Group VIII metal in an amount between 0.01 and 1.0% by weight.
- 30 12. A catalyst of claim 6, characterized in that the catalyst further comprises II-IV metal oxide in an amount of between 0.1 and 20.0% by weight.
- 35 13. A catalyst of claim 6, characterized in that the alkylation catalyst matrix comprises an inorganic porous material.
14. A catalyst of claim 6, characterized in that the alkylation catalyst matrix comprises a porous carbon material.
15. A catalyst of claim 6, characterized in that the catalyst matrix comprises a porous organic material.
- 40 16. An alkylation catalyst of claim 6, characterized in that the catalyst is regenerated with a solvent or a mixture of solvents belonging to different classes of organic compounds, e.g. aromatic hydrocarbons, isoparaffins, oxygen-containing organic compounds, halogen-containing organic compounds or inorganic solvents such as sulfur dioxide, carbon dioxide at temperatures between 50 and 200°C and at pressures of from about 1 to about 100 atm.
- 45
- 50
- 55



\* active component

Fig.1. Distribution of an alkylation catalyst active component on a silica gel support



\* active component

\*\* sibunit

Fig.2. Distribution of an active component on a sibunit support



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/ RU 95/00174

A. CLASSIFICATION OF SUBJECT MATTER C07C 2/58, B01J 31/16, B01J 38/50// (B01J 31/16, 101:50, 103:20, 103:22, 101:30)		
According to International Patent Classification (IPC) or to both national classification and IPC <sup>6</sup>		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 6:C07C 2/58, 2/60, B01J 31/16, 38/50		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A1, 0561284 (INDEMITSU KOSAN COMPANY LIMITED), 22 September 1993 (22.09.93), claims nos 2-6	6-16
A, P	US, A, 5365009 (EXXON RESEARCH AND ENGINEERING COMPANY) 15 November 1994 (15.11.94), claims nos 1,2	6-16
A	US, A, 5191147 (MOBIL OIL CORPORATION), 2 March 1993 (02.03.93), claims nos 4,6	6-16
A	US, A, 5276242 (PHILLIPS PETROLEUM COMPANI), 4 January 1994 (04.01.94), claims nos 1-20	1-5,6-16
A	FR, A1, 2631956 (INSTITUT FRANCAIS DU PETROLE), 1 December 1989 (01.12.89), claims nos 1-6	1-5
A	US, A, 4992615 (MOBIL OIL CORP.), 12 February 1991 (01.02.91), claims nos 1-24	1-5, 6-16
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search 25.10.1995    25 October 1995		Date of mailing of the international search report 10.11.1995    10 November 1995
Name and mailing address of the ISA/ Ru		Authorized officer
Facsimile No.		Telephone No.

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