

[54] **DEHYDRATION CATALYSTS,  
PARTICULARLY FOR THE DEHYDRATION  
OF DIOLS**

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[22] Filed: **July 16, 1973**

[21] Appl. No.: **379,820**

**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 132,892, April 9, 1971, Pat. No. 3,781,222.

[30] **Foreign Application Priority Data**

July 17, 1972 France ..... 72.25770  
Jan. 5, 1973 France ..... 73.00402

[52] U.S. Cl. .... **252/437**, 260/642, 260/681

[51] Int. Cl. .... **B01j 11/82**

[58] Field of Search .... 252/437; 260/681; 423/305,  
423/306

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[57]

**ABSTRACT**

Diol dehydration catalysts and methods of preparing and using the same, constituted at least in part of a pyrophosphate of at least one metal belonging to the group consisting of lithium, sodium, strontium, and barium and possibly of at least one orthophosphate of said metals and including chromium in combined form and/or a basic additive.

**6 Claims, 24 Drawing Figures**

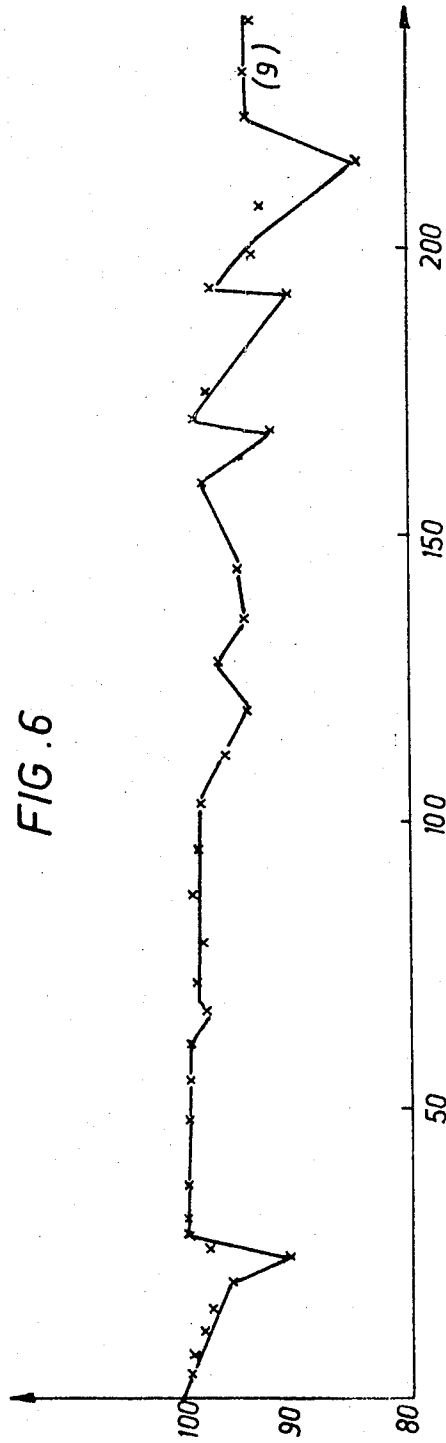
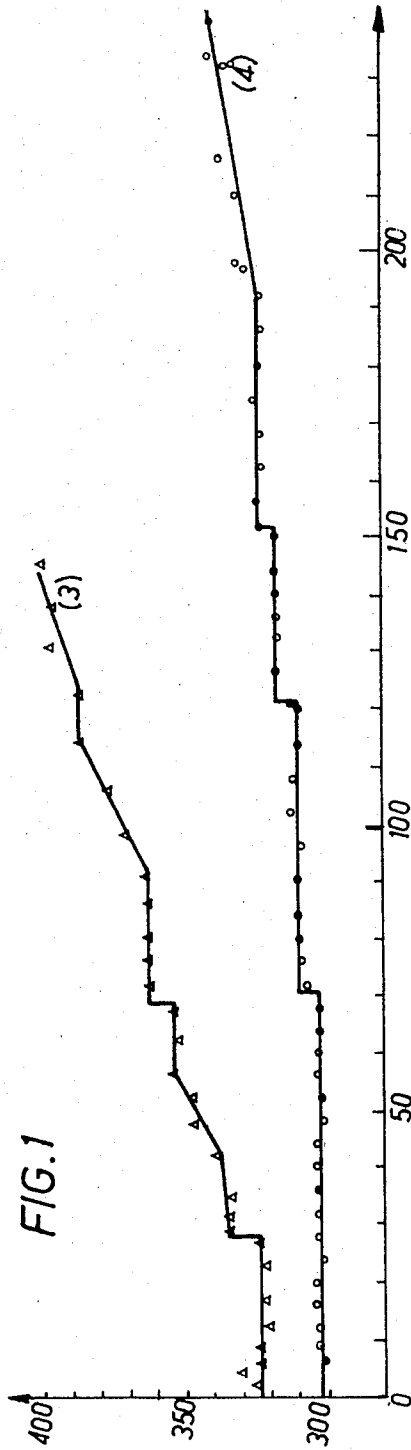
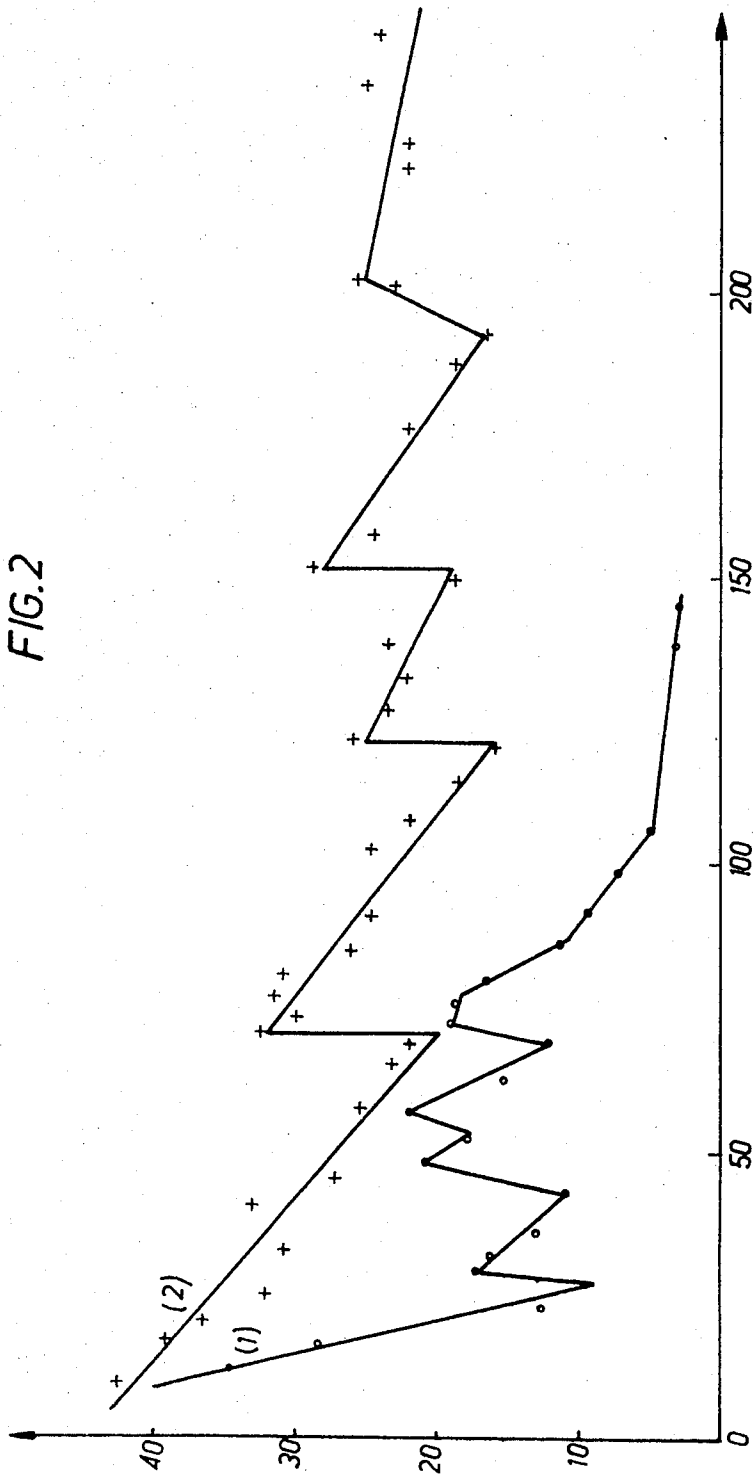
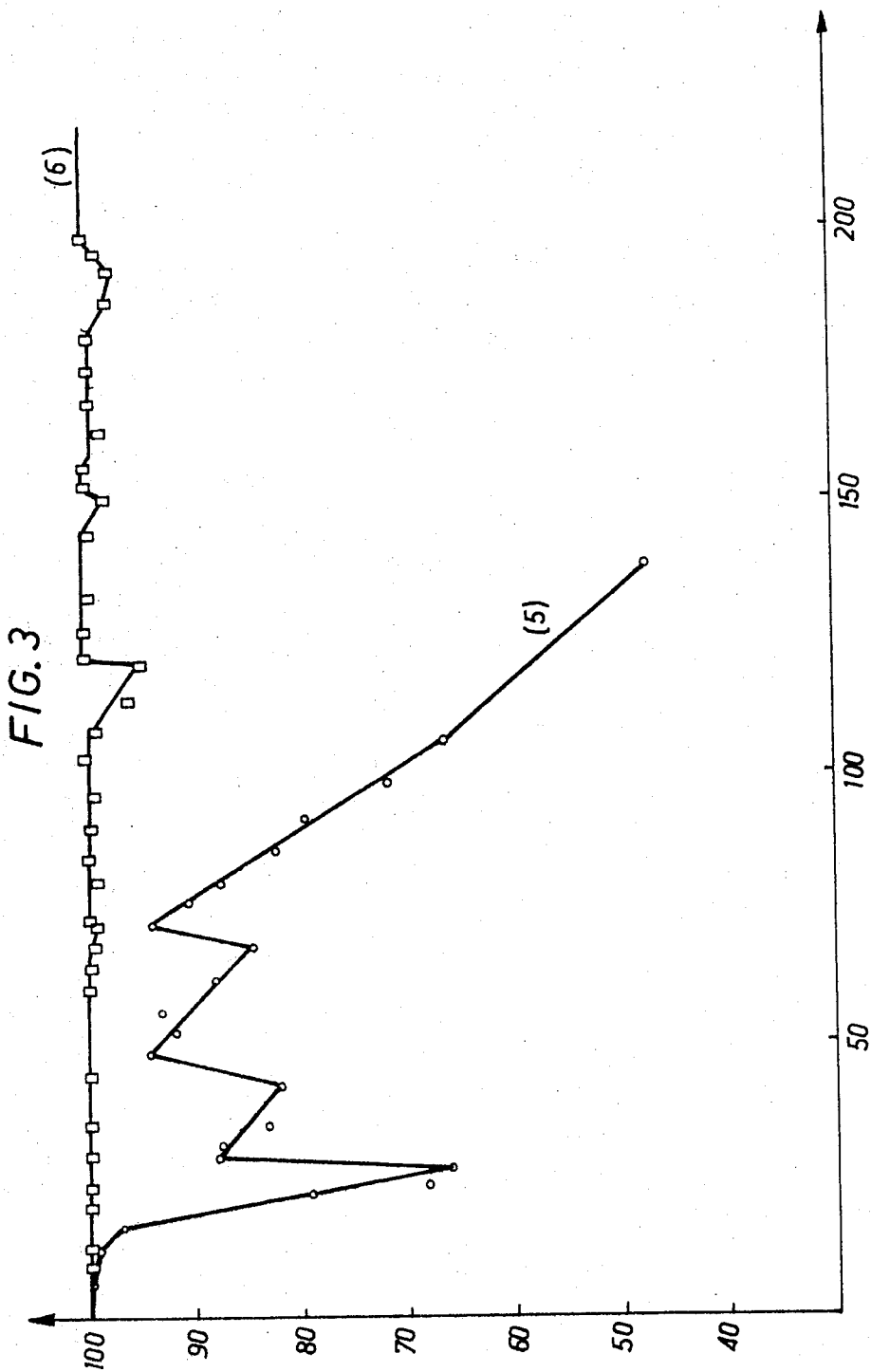
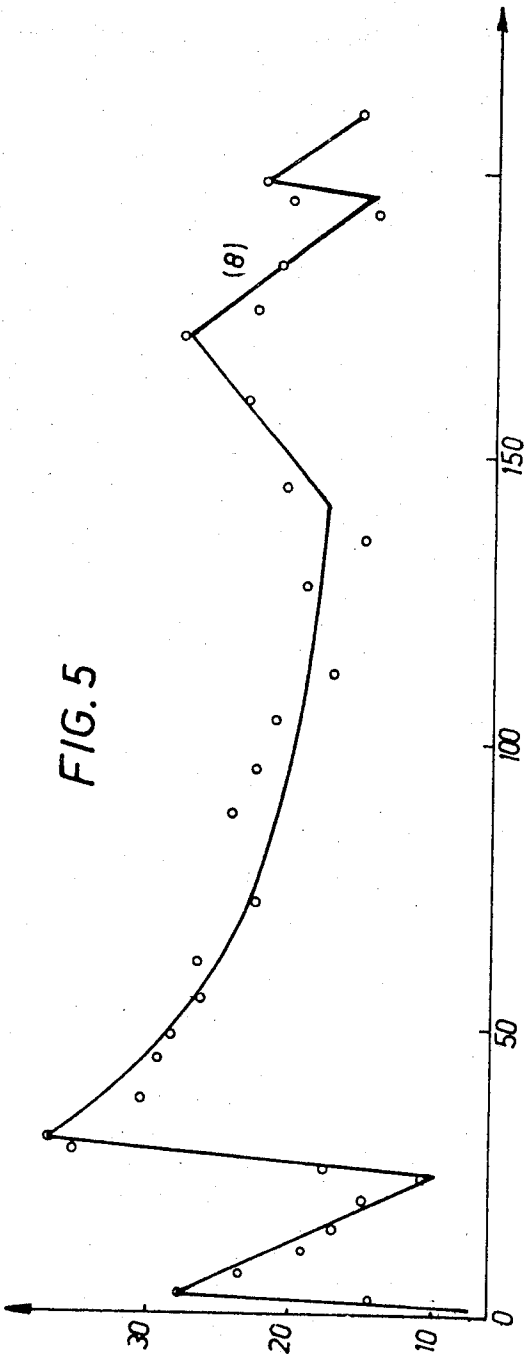
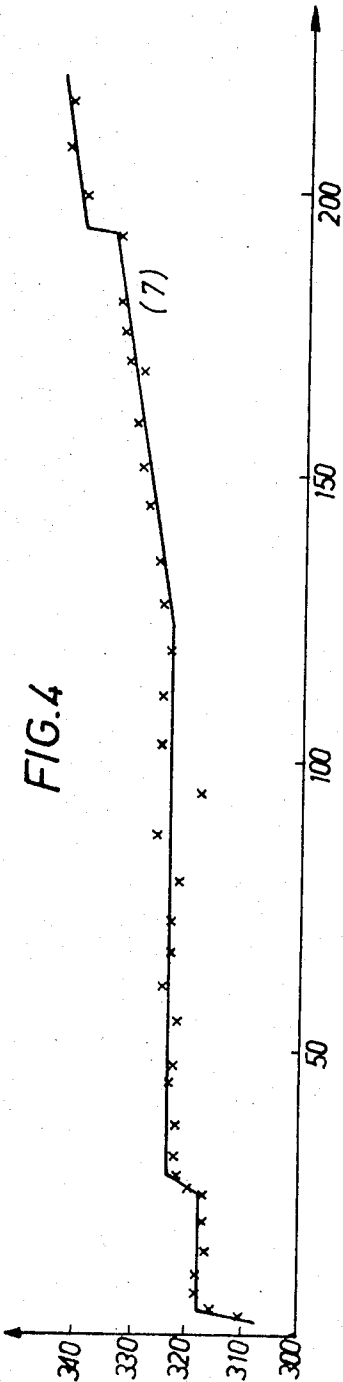
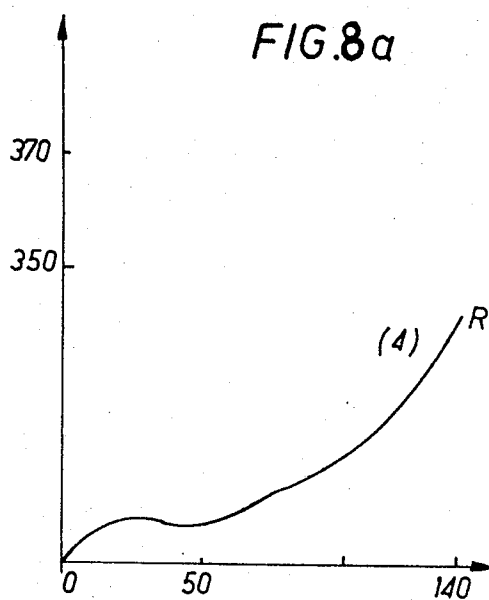
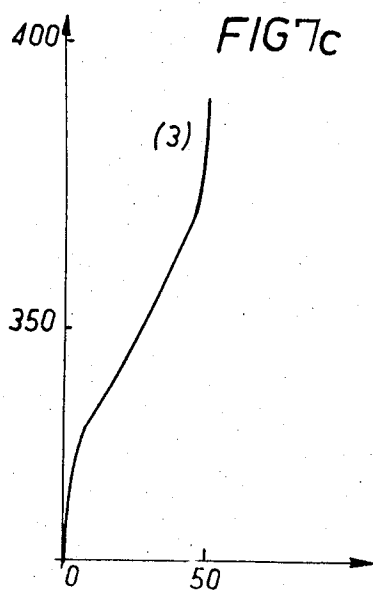
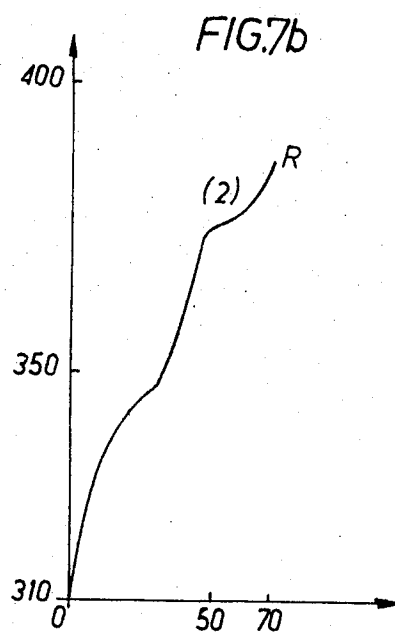
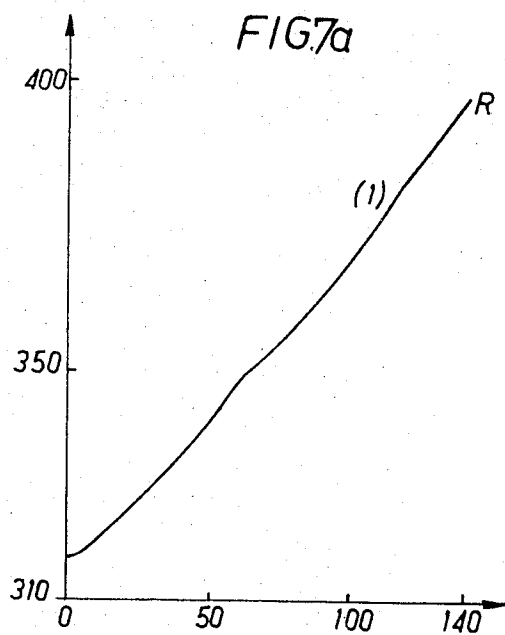


FIG. 2









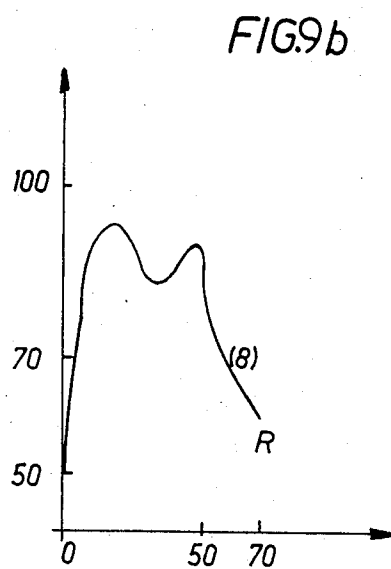
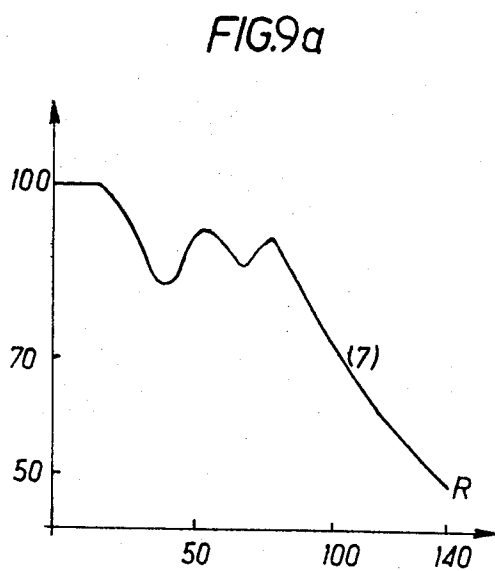
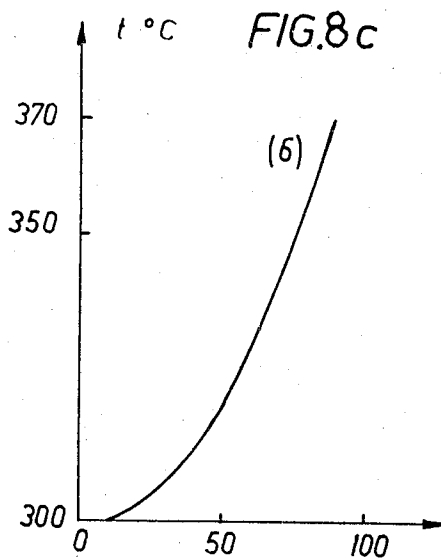
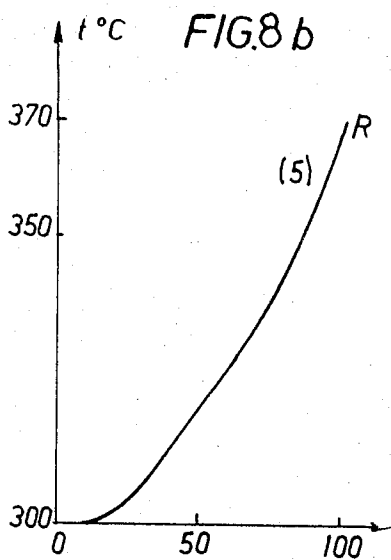


FIG.9c

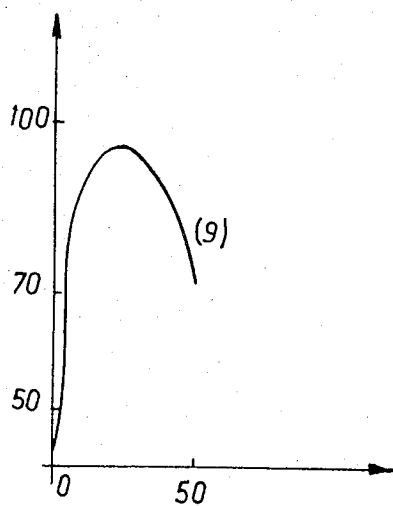


FIG.10a

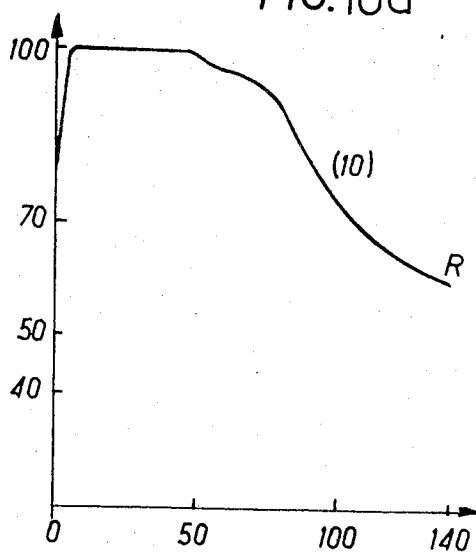


FIG.10b

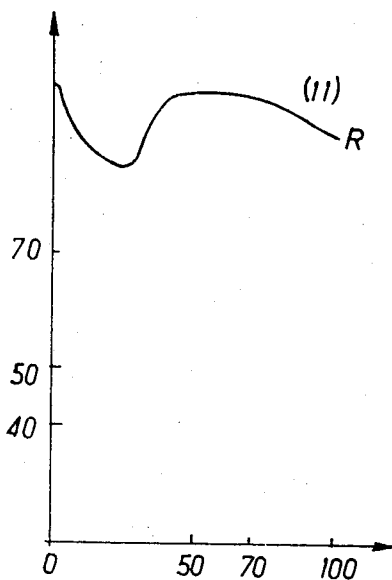
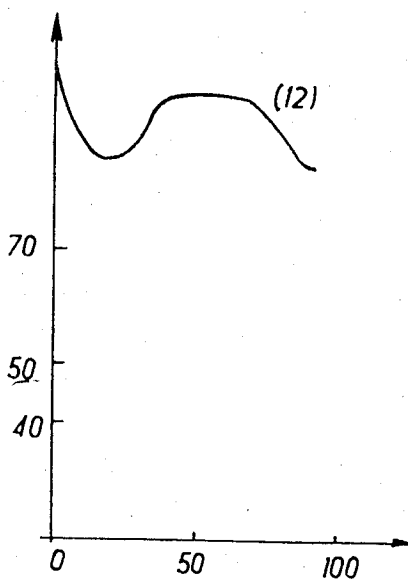
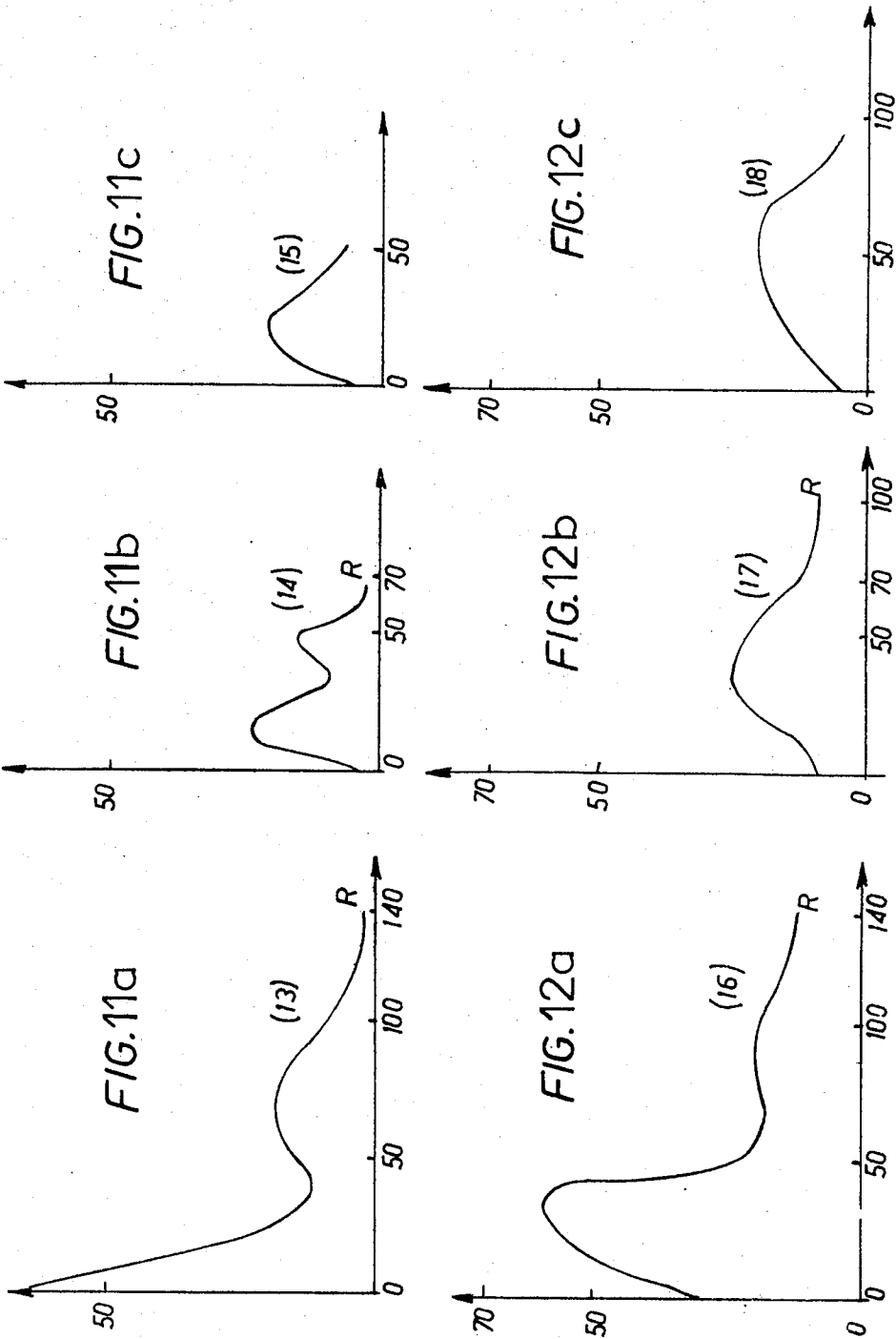


FIG.10c







# DEHYDRATION CATALYSTS, PARTICULARLY FOR THE DEHYDRATION OF DIOLS

This application is a continuation-in-part of application Ser. No. 132,892, filed Apr. 9, 1971, now issued as U.S. Pat. No. 3,781,222, and the latter is hereby incorporated herein in its entirety by reference.

The present invention relates to catalysts for the dehydration of organic compounds. More particularly, it concerns catalysts for the dehydration of diols, which diols may or may not be vicinal. These dehydration catalysts as well as their preparation constitute variants of the catalysts and catalyst preparations which form the object of applicants' aforementioned parent application.

In said application, a dehydration catalyst is described which is characterized by the fact that it is formed, in whole or in part, of at least one mixed or unmixed pyrophosphate, at least one metal belonging to the group formed of:

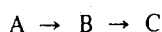
lithium  
sodium  
strontium  
barium

and possibly at least one orthophosphate of at least one metal belonging to the group formed of lithium, sodium, strontium and barium. A process of preparing the catalyst defined above is also described in said patent. Finally, the use of the catalysts of the invention for the dehydration of vicinal or non-vicinal diols is also described therein.

An object of the present application is to describe inventive variants of the catalyst and of the process of preparing it, as well as the use of the newly obtained catalysts to the dehydration of vicinal or non-vicinal diols.

The applicants have found that chromium in combined form and/or a basic additive can advantageously be added to the catalyst forming the object of the parent application, this having the effect of maintaining the activity and the selectivity of the catalyst with the passage of time, as well as the stability of the catalyst after regeneration.

In the following there will be understood by the selectivity of a reaction of the type:



the ratio:

$$S = (\text{Number of mols of B not yet converted into C} + \text{mols of C formed}) / (\text{Number of mols of A consumed})$$

For example, in the case of the dehydration of a diol into diolefin, it is known that one passes through an intermediate compound which is an olefin alcohol. The selectivity of such a reaction is therefore given by the ratio:

$$S = (\text{Number of mols of olefin alcohol and diolefin formed}) / (\text{Number of mols of diol consumed})$$

With regard to the activity of the catalyst, it is known that it may be measured by the velocity constant of the reaction  $A \rightarrow B \rightarrow C$ : the higher this constant, the greater the activity of the catalyst. It can therefore be measured by the conversion of the reagent A, defined by the ratio:

$$C = (\text{Number of mols of A + B consumed}) / (\text{Number of mols of A introduced})$$

Thus for identical times of contact of the reagent with the catalyst (as with identical rates of flow of reagent over the same mass of catalyst), the activities of two different catalysts can be compared.

It is known that it is necessary to regenerate the dehydration catalyst, if it is desired to maintain the activity and the selectivity of the catalyst at acceptable levels without having to raise the reaction temperature too much. These regenerations are carried out by calcining the catalyst in the presence of air and possibly of steam.

The stability of the catalyst characterizes its ability to maintain its selectivity or its activity at satisfactory values with the passage of time.

A preferred embodiment of the present invention is a dehydration catalyst comprising a catalytic composition in accordance with any of the claims of the said parent application, and characterized furthermore by the fact that it contains chromium in combined form and/or a basic additive.

The chromium may, for instance, be present in the form of chromic oxide ( $\text{Cr}_2\text{O}_3$ ) or in the form of chromium phosphate; the amount of chromium expressed as element must be less than or equal to 2% of the total weight of the catalyst.

Another embodiment of the present invention consists of a process of preparing catalysts, which process is characterized by the fact that a chromic oxide powder and/or a basic additive in solid state are mixed with a catalyst composition in accordance with any of the claims of the said parent application, that the catalytic mixture obtained is dried, that it is pelletized or extruded in a suitable die, and that the pellets or extrudates thus obtained are calcined.

Another embodiment of the present invention is a process for the preparation of catalysts, which process is characterized by the fact that mixed or unmixed pyrophosphate, possibly orthophosphate, of a metal belonging to the group consisting of lithium, sodium, strontium and barium, and chromium phosphate are coprecipitated from a single aqueous solution before the shaping and calcining; a basic additive in solid form may possibly be added before the shaping.

The precipitating is effected by a process similar to that described in the said parent application, but in addition one has an initial solution containing a chromium salt, for instance chromic nitrate. The proportions of the different species are obviously defined by the final proportions desired.

The applicants have observed that the beneficial effect of the presence of chromium is felt less when the chromium is present in excessive amount in the catalyst; the selectivity of the latter is affected prior to the first regeneration. The change in the selectivity is not sudden, but it may be said that beyond an addition of about 5% chromic oxide — which corresponds to about 2% chromium calculated as element — the initial loss in selectivity becomes a drawback.

It has been stated that the catalyst of the invention may contain a "basic additive." By "basic additive" there is meant here the hydroxides, oxides and basic salts of a metal belonging to the group consisting of the alkaline or alkaline earth metals, or mixtures of these compounds.

In the various catalytic mixtures produced by the applicants, the proportions of the basic additive added have varied between 0 and 20% by weight. However, while small amounts of basic additive activate the cata-

lyst, too large an amount, on the other hand, deactivates it. The applicants have found that the activation is effective for proportions of basic additive in the catalytic mixture ranging from 0 to 10% by weight approximately.

Upon the mixing of the components of the catalyst, a lubricant can be incorporated which may, for instance, be naphthalene, camphor, stearic acid, or any other product which permits better flow in the pelleting or extrusion die. This lubricant must, however, be capable of being eliminated by evaporation or sublimation at a sufficiently low temperature, without leaving a residue which might orient the dehydration reaction in a different direction; thus, for instance, aluminum stearate will not be used, since it leaves upon calcining traces of alumina on the catalyst. The percentage of lubricant added is not critical; one can, for instance, include 0% to 10% by weight of lubricant in the solid mixture. As a matter of fact, this percentage depends on the machine used for the mechanical treatment. In the case of certain devices — particularly those provided with means capable of vibrating the descent hop-

which therefore contains (depending on the individual case):

90% or 94% pyrophosphate,  
5% or 1% basic additive,  
5% naphthalene.

was mixed and then pelleted and calcined for a first time for about 2 hours at 300°C so as to sublimate the naphthalene, and then a second time for the same period of time at about 500°C.

The catalyst pellets thus obtained were tested for dehydration. The catalyst test consists in passing methyl 2,3-butanediol over 1 cc of catalyst at atmospheric pressure at the rate of 1 cc/hour, measured in liquid state, so as to dehydrate it to isoprene, at a temperature equal to 350°C or 400°C, depending on the tests.

The diol conversion and selectivity results are set forth in Table I below.

The results of Table I show that numerous catalysts obtained by adding a basic additive to the catalyst of the parent application also constitute very good dehydration catalysts.

TABLE I

ADDITIVE	LiOH.H <sub>2</sub> O	CaO	MgO	BaO	SrO	NaOH	None	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	LiOH. H <sub>2</sub> O	NaOH
Wt. %	5	5	5	5	5	5	0	1	1	1	1
Temperature of the catalytic test (°C)	350	350	350	350	350	350	400	400	400	400	400
conversion of the diol	67.4	93.4	61.1	90.5	97.7	96.4	100	99.6	100	99.6	100
Selectivity	80.7	81.4	81.2	80.5	77.6	83.8	80.3	81.7	82.7	82.9	84.1

per for the catalytic mixture — the incorporating of lubricant is unnecessary.

The following examples are not limitative. They illustrate specific embodiments of the preparation of catalysts in accordance with the present invention and their use in dehydration reactions.

The accompanying drawings are also given by way of illustration and not of limitation and merely illustrate the results of the tests reported in the examples.

In the drawings:

FIGS. 1, 2 and 3 are graphs of the results of the tests reported in Example 3,

FIGS. 4, 5 and 6 are graphs of the results reported in Example 4,

FIGS. 7a, 7b, 7c, 8a, 8b, 8c, 9a, 9b, 9c, 10a, 10b, 10c, 11a, 11b, 11c, 12a, 12b, and 12c are graphs of the results of the tests reported in Example 7.

## EXAMPLE I

A double pyrophosphate of lithium and sodium was prepared from aqueous solutions of LiOH and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> by the method of Example 1 of the parent application. This double pyrophosphate was dried at about 110°C and then calcined at 500°C. The resultant mass was crushed and sodium orthophosphate Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O was added to it in a weight ratio of:

(Weight of pyrophosphate)/(Weight of hydrated orthophosphate) = 3/2

By addition of an equal weight of water to the powder there was obtained a paste which was dried at about 110°C in an oven and then crushed. With the crusher used, a particle size of 0.2 to 0.5 mm was obtained.

To the particles thus obtained 5% or 1% by weight of various basic additives indicated in Table I were added. Furthermore, 5% by weight of naphthalene was added to serve for lubrication. The resultant mixture,

## EXAMPLE 2

This example is intended to show the importance of the calcining temperature and its influence on the catalytic properties of various mixtures prepared by the method of Example 1. Only the temperature of the final calcining changes.

The catalytic tests are carried out in the same manner, using as a charge methyl 2,3-butanediol which is passed over 1 cc of catalyst at 350°C at atmospheric pressure, at the rate of 1 cc/hour (rate of flow measured in liquid state).

The conversions and selectivities for different calcining temperatures, with or without additive, will be found in Table II.

TABLE II

Calcining temperature, °C	Conversion of methyl butane-2,3-diol	Selectivity of the dehydration
Catalyst without additive	—350 —400 —450 —500	97.25 99.0 89.9 87.3
Catalyst with 1% by wt. caustic soda	—350 —500	100 100
		81.05 82.7 75.5 75.4 85.45 82.75

## EXAMPLE 3

This example illustrates the use of a catalyst in accordance with the present invention containing 1% caustic soda in accordance with the method of Example 1 above, for the continuous dehydration of methyl bu-

tane-2,3-diol to isoprene for a long period of time. By way of comparison, there is described a test carried out in similar fashion using the preceding catalyst which has not been treated by a basic additive.

A mixture of methyl butane-2,3-diol and 2-methyl 1-butene 3-ol (formed of 30 mol% diol and 70 mol% alpha-olefin alcohol) is passed in a reactor over 40 cc of the catalyst (in particles of 1 to 2 mm), at atmospheric pressure and a temperature which varies in the course of time, and at a rate of 40 cc/hour (rate of flow measured in liquid state).

When the molar percentage of isoprene formed in the efflux becomes too low, it is readjusted by increasing the dehydration temperature. It is known that the ease of dehydration increases with the temperature. This explains the appearance of temperature shoulders in the accompanying figures in which there is plotted, as a function of time:

1. in the case of the dehydration of the diol on the catalyst without additive:

FIG. 1, curve 3/the variation of the average temperature of the reaction

FIG. 2, curve 1/the molar percentage of isoprene in the efflux

FIG. 3, curve 5/the conversion of the diol

2. in the case of the dehydration of the diol on the catalyst treated with 1% by weight caustic soda:

FIG. 1, curve 4/the variation of the average temperature of the reaction

FIG. 2, curve 2/the molar percentage of isoprene in the efflux

FIG. 3, curve 6/the conversion of the diol

From these various curves, it is concluded that with the catalyst containing 1% by weight caustic soda, under the conditions of the test:

the molar percentage of isoprene in the efflux from the reactor is higher

the temperatures at which one operates are definitely lower

the conversion of the diol is maintained in the vicinity of 100

during operation, an identical increase in temperature causes a higher gain in isoprene

the temperature shoulders are longer

#### EXAMPLE 4

This example illustrates the application of catalysts in accordance with the present invention to the continuous dehydration of methyl butane-2,3-diol into isoprene for a prolonged period of time.

The test was carried out in the same manner as in Example 3, with the same charge and with the same quantities.

Only the catalyst was different. It contained 2% of a basic additive which is caustic soda.

In FIGS. 4 and 5 there are plotted as a function of time:

in curve 7: the temperature of the reaction,

in curve 8: the molar percentage of isoprene in the efflux of the reactor.

In FIG. 6 there has been simply shown the variation with time of the conversion of the diol (curve 9).

Examples 5 and 6 are intended to show that the catalysts in accordance with the invention are less sensitive to calcining (which operation is necessary for the regeneration of the catalyst) than catalysts which do not contain chromium in combined form.

Example 7 describes a test on the dehydration of a vicinal diol (methyl butane-2,3-diol) in the presence of a catalyst in accordance with the present invention.

#### EXAMPLE 5

In the present example, the chromium is added in the form of chromic oxide before the pelleting of the catalyst.

A "catalyst 5" is prepared in the following manner:

10.3 liters of a boiling aqueous solution containing 875 g of monohydrated lithia are poured into 5.2 liters of a boiling aqueous solution of sodium pyrophosphate decahydrate containing 2.3 kg of pyrophosphate  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ .

When the supernatant liquid reaches a temperature of 50°C, filtration is effected, followed by washing with 25 liters of water and then drying at a temperature of 120°C. 30 g of the dried product, screened to a size of less than 0.2 mm, and 20 g of disodium orthophosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), screened to a size of less than 0.2 mm, are then mixed together. The mixture is wetted with 50 g of water so as to form a paste which is then dried at a temperature of 120°C. The solid obtained is crushed until obtaining particles of a diameter of between 0.2 and 0.5 mm.

To 40 grams of these grains there are added 0.8 g of chromic oxide ( $\text{Cr}_2\text{O}_3$  which has been previously calcined at a temperature of 1100°C for 16 hours), 2 g of naphthalene, and 2 g of didecyl adipate. They are mixed together and then pelleted. The catalyst thus obtained will hereinafter be referred to as "catalyst 5."

Catalyst 5 is then separated into two lots, one of which is subjected to calcining for 2 hours at a temperature of 550°C, while the other is subjected to calcining for 100 hours at 550°C. The chromic oxide content of catalyst 5 is equal to 2%.

A catalyst 5' containing 5% chromic oxide is prepared by a process similar to that used for the preparation of catalyst 5 but with a larger addition of chromic oxide. Moreover, the calcining of the first lot of catalyst 5' had been effected at 500°C for 2 hours.

A Catalyst T5 containing no chromic oxide was prepared by a process similar to that used for the preparation of catalyst 5, but without addition of chromic oxide.

Each of the two lots of catalysts 5, 5' and T<sub>5</sub> is subjected to a methyl butane-2,3-diol dehydration test — 1 cc, measured in liquid state, of pure diol is passed per hour over 1 cm<sup>3</sup> of catalyst at a temperature of 350°C.

The results obtained with catalysts 5, 5' and T<sub>5</sub> have been entered in Table III below, in which there have been entered the conversion of the diol and the selectivity of the catalyst in question.

TABLE III

Catalyst	Chromic oxide content (%)	Calcining 2 hrs at 550°C		Calcining 100 hrs at 500°C	
		Conversion	Selectivity	conversion	Selectivity
T <sub>5</sub>	0	98.0	77.7	27.1	74.1
5	2	91.05	77.35	75.34	76.5
5'	5	100 <sup>(1)</sup>	78.8 <sup>(1)</sup>	58.9	69.7

<sup>(1)</sup> Catalyst 5' was subjected to calcining for two hours at 500°C and not at 550°C.

The conversion and selectivity of catalyst T<sub>5</sub> decrease much more rapidly than those of catalysts 5 and 5'. It

would also appear that catalyst 5 is stabler than catalyst 5'.

#### EXAMPLE 6

In the present example, the chromium is precipitated simultaneously with mixed sodium-lithium pyrophosphate. A "catalyst 6" is prepared in the following manner:

0.575 liter of a boiling aqueous solution containing 50 grams of lithia monohydrate and 0.060 liter of a boiling aqueous solution containing 22.4 grams of chromic nitrate III nonahydrate are poured simultaneously into 0.350 liter of a boiling aqueous solution containing 157.5 grams of sodium pyrophosphate decahydrate.

After cooling to 50°C, the precipitate is filtered, washed, and then dried at 120°C.

Catalyst 6 is divided into two lots. The first lot is calcined for 2 hours at a temperature of 500°C. The second lot is calcined for 100 hours at a temperature of 550°C.

A catalyst T<sub>6</sub> containing no chromium is prepared by a process similar to that used for the preparation of catalyst 6, but the initial solution of which does not contain chromium nitrate.

Each of the two lots of catalysts 6 and T<sub>6</sub> is subjected to the catalytic test described in Example 5. The results are entered in Table IV. The chromium content, expressed as elemental chromium, of catalyst 6 is equal to 2%.

TABLE IV

Catalyst	Chromium content %	Calcining 2 hrs. at 500°C		Calcining: 100 hours at 550°C	
		Conversion %	Selectivity %	Conversion %	Selectivity %
T <sub>6</sub>	0	98.9	87.5	20.2	68.2
6	2	99.15	79.0	54.8	83.2

The conclusions which can be drawn are the same as those drawn in connection with Example 5, with regard to the comparison of the performances of catalyst T<sub>6</sub> and catalyst 6 of the invention.

#### EXAMPLE 7

A catalyst 7 is prepared by the following method:

2.3 liters of a boiling solution containing 200 grams of lithia monohydrate and 0.240 liters of a boiling aqueous solution containing 89.6 grams of chromic nitrate nonahydrate are poured simultaneously into 1.3 liters of a boiling aqueous solution containing 630 grams of neutral sodium pyrophosphate decahydrate.

The mixture is allowed to cool to 50°C whereupon it is filtered and the precipitate is washed and then dried for 18 hours at 120°C.

117.55 grams of dried precipitate, screened to a size of less than 0.2 mm, and 58.8 grams of disodium orthophosphate (Na<sub>2</sub>HPO<sub>4</sub>·12 H<sub>2</sub>O), screened to a size of less than 0.5 mm, are mixed. The mixture is wetted so as to form a paste which is then dried at a temperature of 120°C. The solid obtained is crushed until obtaining particles of a diameter of between 0.2 and 0.5 mm.

1 gram of Na<sub>2</sub>CO<sub>3</sub>, 5 grams of naphthalene, and 5 grams of didecyl adipate are added to 100 grams of particles obtained. The substances are mixed together and

then pelleted. The pellets are then calcined in a stream of nitrogen, the temperature being slowly increased to 350°C, which temperature is maintained for 2 hours.

A catalyst T<sub>7</sub> containing no chromium is prepared by a method similar to that used for catalyst 7 but, on the one hand, the initial solution does not contain chromium nitrate and on the other hand, no disodium carbonate is added before pelleting.

Catalysts 7 and T<sub>7</sub> are subjected to the following catalytic test: a gaseous mixture formed of 70% (in moles) of 2-methyl 1-butene 3-ol and 30% of 2-methyl butane 2,3-diol, is passed at a pressure of one atmosphere over 25 cm<sup>3</sup> catalyst with an hourly space velocity of the mixture equal to 1, measured in liquid state. When the molar percent of isoprene in the efflux (yield of isoprene) becomes too low, the temperature of the reactor is increased.

After 140 hours of operation, catalysts 7 and T<sub>7</sub> are subject to a first regeneration, which consists in passing a mixture of nitrogen and oxygen — containing 1% oxygen — over the catalyst while it is maintained at a temperature of 450°C until the efflux no longer contains carbon dioxide. At the end of the regeneration, the temperature is slowly brought to 500°C.

The catalysts are then used in a second catalytic test identical to the first, carried out for 70 hours in the case of catalyst T<sub>7</sub> and 100 hours in the case of catalyst 7. At the end of this second use, a second regeneration is effected under the same conditions as the first. Thereupon the catalysts are used for a third time in a catalytic test.

In FIGS. 7a, 7b, 7c, 8a, 8b, 8c, 9a, 9b, 9c, 10a, 10b, 10c, 11a, 11b, 11c, 12a, 12b, and 12c the results obtained have been shown graphically.

In FIGS. 7a, 7b, and 7c, curves 1, 2 and 3 represent the average temperature of the reaction with the use of catalyst T<sub>7</sub>, upon the first use of the catalyst (curve 1), upon the second use after a first regeneration (curve 2), and upon the third use after a second regeneration (curve 3).

In FIGS. 8a, 8b, and 8c, curves 4, 5 and 6 represent the average temperature of the reaction with the use of catalyst 7, upon a first, a second and third use respectively. The letter R designates the moment when the use of the catalyst ceased and when a regeneration was then effected.

In FIGS. 9a, 9b and 9c, curves 7, 8 and 9 represent the conversion of the diol introduced into the reactor upon the first, second and the third use, respectively, of the catalyst T<sub>7</sub>.

In FIGS. 10a, 10b, 10c, curves 10, 11 and 12 are curves similar to curves 7, 8 and 9, but relating to catalyst 7.

In FIGS. 11a, 11b and 11c, curves 13, 14 and 15 represent the molar yield in isoprene upon the use of catalyst T<sub>7</sub>.

In FIGS. 12a, 12b and 12c, curves 16, 17 and 18 are curves similar to curves 13, 14 and 15, but relating to catalyst 7.

These curves show the advantages of catalyst 7 of the invention over catalyst T<sub>7</sub> under the conditions of the test. In Table V below, some of the values which served for the plotting of these curves are indicated

TABLE V

		1st use		2nd use		3rd use	
Catalyst T <sub>7</sub> 0% Cr — 0% Na <sub>2</sub> CO <sub>3</sub>	Time (hours)	50	70	50	70	50	
	Yield of isoprene (%)	15	19	15	3	6	
	Conversion of diol (%)	92	87	79	60	72	
	Temp. (°C)	342	353	375	386	389	
Catalyst 7 1% Na <sub>2</sub> CO <sub>3</sub> 2% Cr	Time (hours)	50	70	50	70	50	70 90
	Yield of isoprene (%)	22	18	16	13	15	12 6
	Conversion of diol (%)	98	95	98	98	98	96 85
	Temp. (°C)	306	310	320	335	320	345 370

A comparison of the performances of the two catalysts in the 3rd use is particularly significant. It is noted that a given yield of isoprene (6%) is obtained after a longer period of use (90 hours instead of 50) with higher conversion at a lower temperature in the case of catalyst 7, although the second regeneration occurred after a longer time of use. Catalyst 7 is therefore more stable than catalyst T<sub>7</sub>.

We claim:

1. In a dehydration catalyst consisting essentially of at least one mixed or unmixed pyrophosphate of at least one metal chosen from the group consisting of lithium, sodium, strontium and barium, the improvement in which said catalyst further consists of a compound of chromium chosen from the group consisting of chromium oxide and chromium phosphate in an amount, expressed as element, which is less than about 2% of the total weight of the catalyst.

2. A dehydration catalyst in accordance with claim 1, further comprising at least one neutral orthophosphate of a metal chosen from the group consisting of lithium, sodium, strontium and barium.

3. In a dehydration catalyst consisting essentially of at least one mixed or unmixed pyrophosphate of at least one metal chosen from the group consisting of lithium, sodium, strontium and barium, the improvement in which said catalyst further consists of a basic additive which is a compound of an alkaline metal or an alkaline earth metal chosen from the group consist-

ing of the hydroxides, oxides, basic salts and mixtures thereof, the percentage of said basic additive in the catalytic mixture finally obtained being less than 10% by weight.

4. A dehydration catalyst in accordance with claim 3, further comprising at least one neutral orthophosphate of a metal chosen from the group consisting of lithium, sodium, strontium and barium.

5. In a dehydration catalyst consisting essentially of at least one mixed or unmixed pyrophosphate of at least one metal chosen from the group consisting of lithium, sodium, strontium and barium, the improvement in said catalyst further consisting of at least one basic additive which is a compound of an alkaline metal or an alkaline earth metal chosen from the group consisting of the hydroxides, oxides, basic salts and mixtures thereof, in an amount less than or equal to 10% of the weight of the catalyst and a compound of chromium chosen from the group consisting of chromium oxide and chromium phosphate in an amount expressed as element less than or equal to about 2% of the total weight of the catalyst.

6. A dehydration catalyst in accordance with claim 5, further comprising at least one neutral orthophosphate of a metal chosen from the group consisting of lithium, sodium, strontium and barium.

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