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SPECIFICATION
POLYOXYMETHYLENE COPOLYMER AND PROCESS FOR
PRODUCING THE COPOLYMER

1 TECHNICAL FIELD

The present invention relates to a polyoxymethylene copolymer. In more particular, the invention relates to a polyoxymethylene copolymer having
5 a specified terminal group composition and excellent in stability and mechanical properties.

BACKGROUND ART

Polyoxymethylenes synthesized by prior art techniques are classified broadly into homopolymers and
10 copolymers. Polyoxymethylene homopolymers and polyoxymethylene copolymers of the prior art respectively have only one of the two desirable characteristics, namely either excellent mechanical property or excellent stability. That is,
15 polyoxymethylene homopolymers obtained by homopolymerization of formaldehyde or trioxane are excellent in mechanical properties but are not satisfactory in stability; on the other hand, polyoxymethylene copolymers obtained by copolymerization
20 of formaldehyde or trioxane with a cyclic ether or cyclic formal are excellent in stability but are poor in mechanical properties. With respect to long term resistance to heat or resistance to hot water,

1 furthermore, even polyoxymethylene copolymers are not
satisfactory.

Polyoxymethylene copolymers are usually
obtained by copolymerizing formaldehyde or trioxane with
5 a cyclic ether. U.S.P. No. 3,027,352 describes a
copolymer obtained by cationically copolymerizing
trioxane with ethylene oxide or 1,4-dioxolane.

Further, U.S.P. No. 3,337,503 discloses the
use of methylal as a molecular weight controlling agent
10 in the polymerization of trioxane. When methylal is
used as the molecular weight controlling agent, the
terminal group of the resulting polymer becomes the
methoxy group.

In the polymerization of formaldehyde or
15 trioxane or the copolymerization thereof with a
comonomer using cationic catalyst, hydride shift (i.e.,
hydrogen abstraction) takes place, which results in
scission of the main chain of the polymer and makes it
impossible to obtain a high molecular weight polymer.
20 Moreover, it is known that the terminals formed by the
scission become the methoxy group and the formate group.

Further, when compounds having hydroxyl
groups, such as water, methanol, formic acid, etc., are
present in polymerization, they function as a chain
25 transfer agent and form unstable terminal structures. A
usually adopted remedial method is to decompose these
unstable structures and stabilize the terminal groups as
hydroxyethoxy groups, by application of post-treatment

1 after polymerization. In the case of formic acid,
however, terminal formate groups are formed
simultaneously.

As described above, in the previous
5 polyoxymethylene copolymers, terminal formate groups are
formed during polymerization by chain transfer reaction
caused by formic acid, which is an impurity in trioxane,
and by hydride shift reaction, which is a side reaction
caused by cationic catalyst, so that it has been
10 difficult to reduce terminal formate groups.

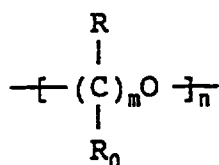
The present invention relates to a
polyoxymethylene copolymer which has both excellent
stability and excellent mechanical property. In more
particular, the invention relates to a polyoxymethylene
15 copolymer which is excellent in stability and mechanical
property and further in long term resistance to heat and
resistance to hot water, and to the process for
producing the same.

DISCLOSURE OF THE INVENTION

20 The present inventors have made extensive
study on the stability of polyoxymethylene. As the
result, they have found that by restricting to a certain
range the amount of inserted oxyalkylene units in
polyoxymethylene copolymer and the amount of terminal
25 formate groups in the copolymer, a polyoxymethylene
copolymer can be obtained which has highly excellent
stability and mechanical property and excellent long

1 term resistance to heat and resistance to hot water.
The present invention has been accomplished on the basis
of above finding.

Thus, the present invention relates to a
5 polyoxymethylene copolymer having a molecular weight of
10,000 - 200,000 which comprises oxymethylene units
(-CH₂O) and oxyalkylene units



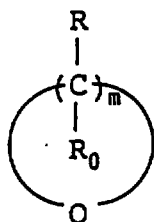
wherein R and R₀ may be the same or different and are
each selected from hydrogen, an alkyl group or an aryl
10 group, n is 1 to 5, and m is 2 to 6, and wherein

(a) the proportion of oxyalkylene units to
oxymethylene units is 0.07 - 0.5% by mole, and

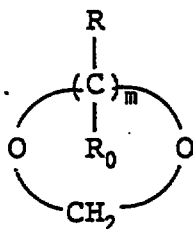
(b) in the infrared spectrophotometry of the
polymer, the ratio of absorbance of terminal formate
15 groups to methylene groups is not more than 0.025.

The present invention will be described in
detail below.

The polyoxymethylene copolymer of the present
invention can be obtained by copolymerization, using a
20 cationic catalyst, formaldehyde or trioxane and a cyclic
ether represented by the formula



- 1 wherein R and R^0 may be the same or different and are
 each selected from hydrogen, an alkyl group or an aryl
 group; further, R bound to different carbon atoms and R_0
 bound to different carbon atoms also may respectively be
 5 the same or different and are selected from hydrogen, an
 alkyl group and an aryl group; and m is 2 to 6,
 or a cyclic formal represented by the formula.



- wherein R and R_0 may be the same or different and are
 selected from hydrogen, an alkyl group or an aryl group;
 10 further, R bound to different carbon atoms and R_0 bound
 to different carbon atoms also may respectively be the
 same or different and are selected from hydrogen, an
 alkyl group or an aryl group; and m is 2 to 6.

As the example of the cyclic ethers used for
 15 obtaining the polymer of the present invention, mention
 may be made of ethylene oxide, propylene oxide, butylene

1 oxide, styrene oxide, etc.

As the example of the cyclic formals, there may be mentioned ethylene glycol formal (1,3-dioxolane), diethylene glycol formal, 1,3-propanediol formal, 1,4-
5 butanediol formal, 1,5-pentanediol formal, 1,6-hexanediol formal, etc. Particularly preferred comonomers are such cyclic formals as ethylene glycol formal (1,3-dioxolane), 1,4-butanediol formal, and the like.

10 The polymer of the present invention can also be obtained by reacting polyacetal homopolymer and a cyclic ether or cyclic formal mentioned above in the presence of a cationic catalyst.

One of the important points in the present
15 invention is the amount of inserted polyalkylene units in the polymer.

Thus, only when the proportion of inserted oxyalkylene units in the polymer is in the range of 0.07-0.5 mole, preferably 0.1-0.3 mole, relative to 100
20 moles of oxymethylene units, a polyoxymethylene copolymer is obtained which is excellent in all of the mechanical property, stability and long term resistance to heat and resistance to hot water. When the proportion of inserted oxyalkylene units is less than
25 0.07 mole, the stability and long term resistance to heat and resistance to hot water become poor. On the other hand, when the proportion of inserted oxyalkylene units exceeds 0.5 mole, the mechanical property becomes

1 markedly poor.

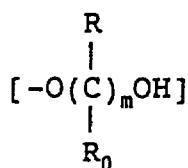
The sequence of oxyalkylene units is also an important point. It is preferable for improving stability, mechanical property, heat resistance and hot water resistance that oxyalkylene units are dispersed in the polymer as individually as possible without forming blocks.

As to n, which represents the sequence of oxyalkylene units, it is preferable that the proportion of n=1 is not less than 95% by mole of the whole oxyalkylene units and the proportion of n≥2 is not more than 5% by mole.

The amount of inserted oxyalkylene units and the sequence mentioned above can be determined by heating and decomposing the polymer in an aqueous 3N HCl solution and analyzing the alkylene glycol, dialkylene glycol and trialkylene glycol in the decomposed solution.

Another important point is the amount of terminal formate in the copolymer.

In the present invention, the terminal groups of the polymer are alkoxy groups such as the methoxy (-OCH₃) group; hydroxyalkoxy groups



1 wherein R and R₀ may be the same or different and are
selected from hydrogen, an alkyl group and an aryl
group; further, R bound to different carbon atoms and R₀
bound to different carbon atoms also may respectively be
5 the same or different and are selected from hydrogen, an
alkyl group and an aryl group; and m is 2 to 6; and
formate groups. Terminal groups other than those
mentioned above, for example hydroxyl groups bound to
oxymethylene units, are very unstable and must be
10 removed by decomposition or converted into hydroxyalkoxy
groups by post-treatment after polymerization, e.g. by
heat decomposition in the presence of an alkaline
substance.

The amount of formate terminal groups in the
15 copolymer can be determined by infrared
spectrophotometry of the film obtained by hot pressing
of the polymer. The absorption wave number (ν) due to
terminal formate is 1710 cm⁻¹ and that due to the
methylene group of polyoxymethylene main chain is 1470
20 cm⁻¹. The amount of terminal formate groups in the
copolymer can be expressed by the ratio of these
absorbances, D_{1710}/D_{1470} .

The amount of formate groups in the copolymer
of the present invention should be not more than 0.025,
25 preferably not more than 0.020, in terms of D_{1710}/D_{1470} .
When D_{1710}/D_{1470} is higher than the value, the stability,
heat resistance and hot water resistance of the
copolymer are deteriorated.

1 Thus, only when the polyoxymethylene copolymer
meets the requirements for the amount of inserted
oxyalkylene units and the amount of terminal formate
groups specified above, the copolymer has excellent
5 stability, mechanical property and long term resistance
to heat and resistance to hot water.

Suitable cationic polymerization catalysts
used for obtaining the polymer of the present invention,
that is, a polyoxymethylene copolymer having a specified
10 amount of terminal formate groups and excellent in
stability, mechanical property and long term resistance
to heat and resistance to hot water, are perfluoroalkyl-
sulfonic acids or their derivatives. As specific
examples, mention may be made of trifluoromethane-
15 sulfonic acid, pentafluoroethanesulfonic acid,
heptafluoropropanesulfonic acid, nonafluorobutane-
sulfonic acid, undecafluoropentanesulfonic acid,
perfluoroheptanesulfonic acid, etc.; and, as
derivatives, super-strong acid anhydrides such as
20 trifluoromethanesulfonic acid anhydride, pentafluoro-
ethanesulfonic acid anhydride, heptafluoropropane-
sulfonic acid anhydride, nonafluorobutane sulfonic acid
anhydride, undecafluoropentanesulfonic acid anhydride,
perfluoroheptanesulfonic acid anhydride, etc.; alkyl
25 esters of super-strong acids such as methyl
trifluoromethanesulfonate, ethyl trifluoromethane-
sulfonate, ethyl pentafluoroethanesulfonate, methyl
pentafluoroethanesulfonate, methyl heptafluoropropane-

1 sulfonate, etc.; and alkylsilyl esters of super-strong
acids such as trimethylsilyl trifluoromethanesulfonate,
triethylsilyl trifluoromethanesulfonate; and the like.

Catalysts conventionally used in

5 polymerization or copolymerization of trioxane are Lewis
acids, such as boron trifluoride, tin tetrachloride,
titanium tetrachloride, phosphorus pentafluoride, and
phosphorus pentachloride, and the compounds or the salts
thereof. When these catalysts are used, however,
10 hydride shift, which is a side reaction in
polymerization, occurs to a large extent, and the amount
of terminal formate groups in the resulting copolymer
can satisfy the condition of D_{1710}/D_{1470} being not more than
0.025 with much difficulty. Further, these catalysts
15 are insufficient in polymerization activity and cannot
achieve a satisfactory polymerization unless the
catalysts are used in a high concentration.
Consequently, the resulting polymer contains a high
concentration of residual catalyst and hence has a low
20 heat stability. Therefore, a complicated process
becomes necessary including the washing and removal of
the catalyst after polymerization.

The concentration of the catalyst in the
present invention should be in the range from 1×10^{-6} to
25 2×10^{-5} % by mole relative to the principal monomer. At
concentrations lower than said range, no polymerization
takes place. At concentrations higher than the range,
the catalyst remaining in the polymer will cause

1 depolymerization, which results in low heat stability of the polymer.

Thus, the present inventors have found that when perfluoroalkylsulfonic acids or their derivatives
5 are used as the catalyst, hydride shift, which is a side reaction in polymerization, can be suppressed and a polyoxymethylene copolymer which satisfies the condition of D_{1710}/D_{1470} being not more than 0.025 can be obtained.

Furthermore, the present inventors have found
10 that when perfluoroalkylsulfonic acids or their derivatives are used as the catalyst, the amounts of water and formic acid contained in the monomer greatly affect the polymerization activity of the catalyst. That is, in the present invention, the concentrations of
15 water and formic acid in the monomer must respectively be not more than 40 ppm. When the concentrations are higher than 40 ppm, the polymerization activity lowers markedly. When the catalyst concentration is in the range from 1×10^{-6} to 2×10^{-5} % by mole relative to the
20 principal monomer, polymerization does not start at all, or gives a very low polymerization yield, which is unpractical.

Molecular weight controlling agents preferably used in the polymerization are alcohols and ethers.
25 Particularly preferred are alkyl ethers, such as methylal and the like. Water, formic acid, methyl formate, etc., also act as a molecular weight controlling agent besides those mentioned above. In the

1 present invention, however, particularly water and
formic acid cannot be used because of their effect on
catalyst activity described above. Methyl formate also
is unpreferable since it forms terminal formate groups.
5 Therefore, when water, formic acid, or methyl formate is
contained as impurities in the monomer, the amounts of
these impurities must be reduced as much as possible by
purifying the monomer in advance of polymerization.

The molecular weight of the polymer of the
10 present invention should be in the range from 10,000 to
200,000. When the molecular weight is not more than
10,000, a satisfactory mechanical property cannot be
obtained. On the other hand, when the molecular weight
is not less than 200,000, processability of the polymer,
15 such as moldability and extrudability, is markedly poor,
which is unpractical.

The polymerization apparatus used in the
present invention may be either a batch-wise one or a
continuous one and is not particularly limited. As a
20 batch-wise polymerization apparatus, there may generally
be used a reaction vessel equipped with a stirrer. As a
continuous apparatus, there may be used self-cleaning
type blenders, e.g., Ko-Kneaders, twin-screw continuous
extruder-blenders and double shaft, paddle type
25 continuous blenders. The polymerization temperature may
be 60-200°C, preferably 60-140°C. The polymerization
time is not particularly restricted but generally
selected from the range of not less than 10 seconds and

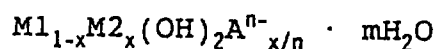


1 not more than 100 minutes.

After polymerization, the catalyst is usually deactivated since the catalyst contained in the polymer produced causes depolymerization. The deactivation is
 5 generally conducted by contacting the polymer with an aqueous solution or an organic solvent containing a basic substance such as triethylamine or by adding and melt-blending a basic substance with the polymer to neutralize and deactivate the catalyst. The present
 10 inventors have made extensive study on the methods of deactivating the polymerization catalyst and resultantly found, as an utterly novel method, a highly effective method in which deactivation is conducted by adding and melt-blending with the copolymer a crystalline acidic
 15 adsorbent comprising at least two kinds of metal oxides or metal hydroxides. In more particular, to 100 parts by weight of polyoxymethylene copolymer, there is preferably added and melt-blended 0.001-0.5% by weight, more preferably 0.005-0.1% by weight, of at least one
 20 adsorbent selected from

a) ion adsorbents comprising at least two kinds of oxides selected from alkali metal oxides, alkaline earth metal oxides, and oxides of trivalent and tetravalent elements, or

25 b) ion adsorbents represented by the formula



- 1 wherein M1 denotes at least one divalent metal selected from alkaline earth metals; M2 denotes a trivalent metal; A^{n-} denotes an n-valent anion; x is a number satisfying $0 < x \leq 0.5$; and m is a positive number. The
- 5 alkali metal oxide may be Na_2O , K_2O and the like. The alkaline earth metal oxide may be MgO , CaO and the like. The trivalent and tetravalent element oxide may be Al_2O_3 , SiO_2 , TiO_2 and the like. Specific examples of the ion adsorbent comprising at least two types of oxides
- 10 selected from these oxides include $2.5 MgO \cdot Al_2O_3 \cdot nH_2O$, $2MgO \cdot 6SiO_2 \cdot nH_2O$, $Al_2O_3 \cdot 9SiO_2 \cdot nH_2O$, $Al_2O_3 \cdot Na_2O \cdot 2CO_3 \cdot nH_2O$, $Mg_{0.7}Al_{0.3}O_{1.15}$, and the like. In the above formula $Ml_{1-x}M2_x(OH)_2A^{n-}_{x/n} \cdot mH_2O$, examples of M1 include Mg, Ca etc., examples of M2 include B, Al, Ga, In, Ti, Tl etc., and
- 15 examples of A^{n-} include CO_3^{2-} , OH^- , HCO_3^- , $H_2PO_4^-$, NO_3^- , I^- , salicylate ion, citrate ion, tartrate ion, etc. Particularly preferred examples are CO_3^{2-} and OH^- . Specific examples of ion adsorbent of this kind are natural hydrotalcite represented by
- 20 $Mg_{0.75}Al_{0.25}(OH)_2CO_3 \cdot 0.125 \cdot 0.5H_2O$ and synthetic hydrotalcite represented by $Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5H_2O$ or similar formulas.

The amount of these deactivating agents to be added is preferably 0.001-0.5% by weight, more preferably 0.005-0.1% by weight, relative to the

25 polymer. When the amount is not more than 0.001% by weight the polymerization catalyst is not deactivated sufficiently. When the amount is not less than 0.5% by weight, discoloration occurs during molding and the

1 color tone of the molded article becomes poor. The
particle diameter of the deactivating agent is not
particularly limited, but is preferably not more than
100 μ m to attain enhanced dispersibility. Further, the
5 deactivating agent may be surface-treated to improve the
dispersibility into the polymer.

The deactivating agent may be added by feeding
it to the polymerization reactor after completion of
polymerization or, in a continuous polymerization
10 reactor, by feeding it to the latter stage of the
reactor, or by adding and mixing it with the polymer
discharged from the reactor. The polymer to which the
deactivating agent has been added may be further melt-
blended to deactivate the polymerization catalyst more
15 thoroughly. The melt-blending is conducted in the
temperature range from the melting point of the polymer
to 270°C. The melt-blending apparatus may be, for
example, single screw type continuous extruder,
Ko-Kneader, twin-screw type continuous extruder, etc.

20 When the copolymer obtained has an unstable
terminal hydroxyl group, the unstable part is decomposed
and removed by conventional methods, for example, by
heat-treating the copolymer with a basic substance, such
as an aqueous triethylamine solution. This operation
25 can be conducted simultaneously with the operation of
adding and melt-blending the deactivating agent of the
catalyst or in the same melt-blending apparatus as used
for the above deactivating operation.

1 Example

The present invention will be described in more detail below with reference to Examples, but the invention is in no way limited by the Examples.

5 The items of determination shown in the Examples are as follows.

1. Terminal formate: The copolymer is hot-pressed at 200°C to form film of 15 μm thickness. The infrared absorption spectrum of the film obtained is
10 taken, from which the ratio of absorbance at $\nu = 1710\text{ cm}^{-1}$ to absorbance at $\nu = 1470\text{ cm}^{-1}$, D_{1710}/D_{1470} , is calculated.
2. Inserted amount and sequence of oxyalkylene units: Ten grams of the copolymer is put in 100 ml of
15 aqueous 3N HCl solution and is decomposed by heating the solution in a tightly sealed vessel at 120°C for 2 hours. After cooling, the amounts of alkylene glycol, dialkylene glycol and trialkylene glycol in the aqueous solution are determined by gas chromatography (FID), and
20 the amount of oxyalkylene units is expressed in terms of % by mole relative to the oxyalkylene units in the copolymer.

As to the sequence of oxyalkylene units, the amount of monoalkylene glycol corresponds to $n=1$, the
25 amount of dialkylene glycol to $n=2$ and the amount of trialkylene glycol to $n=3$.

3. MI: This is determined in accordance with ASTM D-1238-86.

1 4. Heat stability: Resin is retained in an
injection molding machine (Arburg All-rounder 100, a
trade name, mfd. by Western Trading K.K.) at a cylinder
temperature of 230°C and then formed into test pieces of
5 12 by 120 by 3 mm. The time at which a silver streak
develops on the test piece surface is determined. The
higher the value of the time is, the more excellent is
the heat stability of the polymer.

5. Resistance to heat aging: Test pieces in
10 accordance with ASTM D-638 are held in a Geer Oven (type
GPS-222, mfd. by Tabai ESPEC CORP.) at 240°C and then
examined for retention of tensile strength.

6. Resistance to hot water: Test pieces in
accordance with ASTM D-638 are immersed in hot water
15 (flowing water) adjusted to 120°C and then examined for
retention of tensile strength.

Note) Description of abbreviations in the Tables

A-1: trifluoromethanesulfonic acid

A-2: trifluoromethanesulfonic acid anhydride

20 A-3: methyl trifluoromethanesulfonate

A-4: trimethylsilyl trifluoromethanesulfonate

A-5: boron trifluoride dibutyl etherate

B-1: $Mg_{0.75}Al_{0.25}O_{1.125}$

B-2: $Al_2O_3 \cdot Na_2O \cdot 2CO_3 \cdot H_2O$

25 B-3: $Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3H_2O$

B-4: $Al_2O_3 \cdot 9SiO_2 \cdot H_2O$

B-5: triethylamine

C-1: 1,3-dioxolane

- 1 C-2: 1,3-propanediol formal
 C-3: 1,4-butanediol formal
 C-4: 1,6-hexanediol formal
 C-5: ethylene oxide

5 Example 1

 Two thousand grams of a highly purified trioxane (containing 2 ppm of water and 3 ppm of formic acid), 0.8% by mole per trioxane of 1,3-dioxolane and 0.2% by mole per trioxane of methylal were placed in a
10 jacketed kneader having two Σ -shaped blades and the mixture is heated to 70°C. Then a dioxane solution of trifluoromethanesulfonic acid (0.002 mol/l) is added so as to give a proportion of trifluoromethanesulfonic acid to trioxane of 5×10^{-6} % by mole, and the resulting
15 mixture is allowed to polymerize. Fifteen minutes after the initiation of polymerization, cold water is put into the jacket and the reaction mixture is cooled under nitrogen atmosphere. After 1 hour, the content of the kneader is taken out, and $Mg_{0.75}Al_{0.25}O_{1.125}$ (Kyowaad KW2300, a trade name, mfd. by Kyowa Chemical Industry) is added
20 as a deactivating agent in a proportion of 0.01% by weight relative to the polymer obtained, and the resulting mixture is extruded at 200°C with a vent-type twin-screw extruder. Further, 1 part by weight of
25 triethylamine, 5 parts by weight of water, and 0.2 part by weight of 2,2-methylenebis(4-methyl-6-t-butylphenol) are added to 100 parts by weight of the polymer extruded

1 above and the mixture is extruded with a vent-type image
screw extruder (extrusion temperature: 200°C, vent
pressure: 200 torr). The copolymer thus obtained is
evaluated for its terminal formate, amount of inserted
5 oxyalkylene units, sequence of oxyalkylene units, MI,
heat stability, resistance to heat aging and resistance
to hot water. The results are shown in Table 1 and 2.

The polymerization yield is as high as 89% and
 D_{1710}/D_{1470} , which represents the amount of terminal formate
10 groups, is as low as 0.01. With regard to oxyalkylene
units, the amount of diethylene glycol relative to the
amount of ethylene glycol is as low as 0.3% by mole.

With regard to the properties of the polymer,
heat stability is good and tensile strength was
15 excellent. Further, resistance to heat aging and
resistance to hot water are both good, the retentions of
tensile strength after the lapse of 2000 hours being 80%
or more in both tests.

Examples 2 to 18

20 Polyoxymethylene copolymers are synthesized in
the same manner as in Example 1 except for changing the
amounts of catalyst, water and formic acid in the
monomer, 1,3-dioxolane and methylal and/or varying the
type of comonomer and other conditions as shown in Table
25 1. The polymers obtained are treated and evaluated
respectively in the same manner as in Example 1. The
results are shown in Tables 1 and 2. Similarly to the

1 results in Example 1, all the copolymers showed a high
polymerization yield and a low content of terminal
formate groups. Also, they showed a good heat stability
and an excellent tensile strength. Further, the
5 copolymers were excellent both in resistance to heat
aging and in resistance to hot water, the retentions of
tensile strength after the lapse of 2,000 hours being
both 80% or more.

Examples 19 to 23

10 Polyoxymethylene copolymers are synthesized in
the same manner as in Example 1 except for changing the
type of catalyst, the amount of catalyst and other
conditions as shown in Table 1. The polymers obtained
are treated and evaluated respectively in the same
15 manner as in Example 1. The results are shown in Tables
1 and 2. Similarly to the results in Example 1, all the
copolymers showed a high polymerization yield and a low
content of terminal formate groups. Also, they showed a
good heat stability and an excellent tensile strength.
20 Further, the copolymers are excellent both in resistance
to heat aging and in resistance to hot water, the
retentions of tensile strength after the lapse of 2,000
hours being both 80% or more.

Comparative Example 1

25 A polyoxymethylene copolymer was synthesized
by using the apparatus of Example 1 and in the same

- 1 manner as in Example 1 except that boron trifluoride
dibutyl etherate (0.02 mol/l benzene solution) is used
as the polymerization catalyst and the catalyst
concentration is changed to 5×10^{-3} % by mole relative
5 to trioxane. The polymer taken out from the kneader was
melt-blended with a deactivating agent in the same
manner as in Example 1. The resulting polymer is
treated and evaluated respectively in the same manner as
in Example 1. The results are shown in Tables 1 and 2.
10 The polymer showed a high value of terminal formate
amount of 0.045 in terms of D_{1710}/D_{1470} . It showed a heat
stability of 48 min, which is markedly lower as compared
with the values in Examples. The copolymer is poor both
in resistance to heat aging and in resistance to hot
15 water as compared with the polymers of Examples, the
retention of tensile strength after the lapse of 2,000
hours being 60% or less.

Comparative Examples 2 to 8

- Polyoxymethylene copolymers are synthesized by
20 using the apparatus of Example 1 and in the same manner
as in Example 1 but under the conditions shown in Table
1. Under the conditions of Comparative Examples 3 and
4, the polymerization activity is insufficient and no
polymer could be obtained. Under other conditions,
25 polymers could be obtained although the polymerization
yields are lower than in Examples. The polymers
obtained are treated and evaluated respectively in the

1 same manner as in Comparative Example 1. The results
are shown in Tables 1 and 2. All the polymers showed a
high value of terminal formate group amount of 0.040 or
more in terms of D_{1710}/D_{1470} . Also, they showed a heat
5 stability of 50 min or less, which is markedly lower
than in Examples. Further, they are poor both in
resistance to heat aging and in resistance to hot water,
the retentions of tensile strength after the lapse of
2,000 hours being both 50% or less.

10 Comparative Examples 9 and 10

Polyoxymethylene copolymers are synthesized by
using the apparatus of Example 1 and in the same manner
as in Comparative Example 1 but under the conditions
shown in Table 1. Thirty minutes after the initiation
15 of polymerization, 1 l of an aqueous 5% by weight
triethylamine solution is added to deactivate the
polymerization catalyst and terminate the
polymerization. The polymer obtained is collected by
filtration and dried by heating under a nitrogen gas
20 stream at 135°C. Then, to 100 parts by weight of the
polymer thus obtained were added 1 part by weight of
triethylamine, 5 parts by weight of water and 0.2 part
by weight of 2,2-methylenebis(4-methyl-6-t-butylphenol)
and the resulting mixture is extruded with a vent-type
25 single screw extruder (extrusion temperature: 200°C,
vent pressure: 200 torr).

The polymers thus obtained are evaluated in

1 the same manner as in Example 1. The results are shown
in Tables 1 and 2. The copolymers showed a high value
of terminal formate group amount of 0.040 or 0.044 in
terms of D_{1710}/D_{1470} . Also, they showed a heat stability of
5 35 min or 40 min, which are markedly lower than in
Examples. Further, the polymers are very poor both in
resistance to heat aging and in resistance to hot water,
the determination of tensile strength after the lapse of
2,000 hours being impossible.

10 Comparative Examples 11 to 16

Polyoxymethylene copolymers are synthesized by
using the apparatus of Example 1 and under the same
conditions as in Example 1 except for changing the
amount of trifluoromethanesulfonic acid of
15 polymerization catalyst and the moisture content and the
formic acid concentration in the monomer. The results
are shown in Tables 1 and 2. At a catalyst
concentration of 1×10^{-6} % by mole relative to trioxane,
no polymer could be obtained. Also, at catalyst
20 concentrations of 2×10^{-5} to 5×10^{-5} % by mole relative
to trioxane, no polymer could be obtained or
polymerization yield is very poor, when the amount of
water or formic acid in the monomer is 50 ppm or more.
Further, at a catalyst concentration of 5×10^{-5} % by
25 mole relative to trioxane, the polymer obtained is very
poor in heat stability, resistance to heat aging, and
resistance to hot water.

1 Comparative Examples 17 to 20

Polyoxymethylene copolymers are synthesized by using the apparatus of Example 1 and under the same conditions as in Example 1 except for changing the amount of comonomer. The polymers thus obtained are treated and evaluated respectively in the same manner as in Example 1. The results are shown in Tables 1 and 2. When the amount of inserted oxyalkylene units in the polymer is 0.05% by mole or less, the resulting polymer is markedly poor in heat stability, resistance to heat aging, and resistance to hot water. On the other hand, when the amount of inserted oxyalkylene units in the polymer is 0.6% by mole or more, the polymer showed a markedly low tensile strength.

15 Examples 24 to 26

A continuous blending reactor (KRC-Kneader, a trade name, mfd. by Kurimoto Limited) comprised of a barrel of L/D of 14 having a cross section of partially overlapping circles of 50 mm inside diameter and equipped on the outside with a jacket through which a heating medium can be passed, and of two rotating shafts provided inside the barrel and having a number of paddles which engage with one another is used. At a jacket temperature of 80°C and a number of rotation of 78 rpm, trioxane (2 kg/hour), 1,3-dioxolane (3 levels of 0.3, 0.8 and 1.4% by mole relative to trioxane), methylal (0.3% by mole relative to trioxane) and a

1 dioxane solution (0.002 mole/l) of
trifluoromethanesulfonic acid are fed continuously into
the reactor so as to give a proportion of
trifluoromethanesulfonic acid to trioxane of 1×10^{-5} %
5 by mole, to effect polymerization. The polymer
discharged from the polymerization reactor is taken out
under nitrogen atmosphere, then $Mg_{0.75}Al_{0.25}O_{1.125}$ (Kyowaad
KW2300, a trade name, mfd. by Kyowa Chemical Industry)
was added as a deactivating agent to the polymer in a
10 proportion of 0.01% by weight to the polymer, and the
resulting mixture is extruded with a vent-type twin-
screw extruder at 200°C. To 100 parts by weight of the
polymer thus obtained are added 1 part by weight of
triethylamine, 5 parts by weight of water and 0.2 part
15 by weight of 2,2-methylenebis(4-methyl-6-t-butylphenol)
and the mixture is extruded with a vent-type single
screw extruder (extrusion temperature: 200°C, vent
pressure: 200 torr). The copolymers thus obtained are
evaluated in the same manner as in Example 1. The
20 results are shown in Tables 1 and 2. All the polymers
showed a high polymerization yield and a low amount of
terminal formate groups. They showed a good heat
stability and excellent tensile strength. Further, the
copolymers are excellent both in resistance to a heat
25 aging and in resistance to hot water, the retentions of
tensile strength after the lapse of 2,000 hours being
80% or more.

1 Examples 27 to 31

 Polyoxymethylene copolymers are synthesized under the same conditions as in Example 25. Then, the deactivating agents shown in Table 1 were added to the
5 copolymers, as a deactivating agent used after polymerization, in amounts shown in Table 1, and melt-blended in the same manner as in Example 25. The resulting polymers are treated and evaluated respectively in the same manner as in Example 25. The
10 results are shown in Tables 1 and 2. All the copolymers showed a good heat stability and tensile strength as in Example 1. Further, the copolymers were excellent both in resistance to heat aging and in resistance to hot water, the retentions of tensile strength after the
15 lapse of 2,000 hours being 80% or more.

 Comparative Examples 21 to 25.

 Polyoxymethylene copolymers are synthesized in the same manner as in Example 1 but under the conditions shown in Table 1.

20 The copolymers are treated in exactly the same manner as in Example 25 except that the copolymers are taken out from the polymerization reactor under a nitrogen atmosphere containing 1% by volume of air, to obtain polyoxymethylene copolymers. The polymers
25 obtained were evaluated in the same manner as in Example 25. The results are shown in Tables 1 and 2. The polymers obtained all showed a terminal formate group

- 1 content of 0.03 or more in terms of D_{1710}/D_{1470} . The
polymers were all poorer both in resistance to heat
aging and in resistance to hot water than those of
Examples, the retentions of tensile strength after the
5 lapse of 2,000 hours being 60% or less.

Table 1-1

	Poly- meriza- tion catalyst	Catalyst concen- tration (mol %)	Water in monomer (ppm)	Formic acid in monomer (ppm)	Comono- mer	Comono- mer amount (mol %)	Deacti- vating agent	Amount of deactivating agent added (phr)
Example-1	A-1	5.0×10^{-6}	2	3	C-1	0.8	B-1	0.01
Example-2	A-1	5.0×10^{-6}	5	10	C-1	0.8	B-1	0.01
Example-3	A-1	1.0×10^{-5}	11	8	C-1	0.8	B-1	0.01
Example-4	A-1	1.0×10^{-5}	18	19	C-1	0.8	B-1	0.01
Example-5	A-1	2.0×10^{-5}	26	8	C-1	0.8	B-1	0.01
Example-6	A-1	2.0×10^{-5}	12	22	C-1	0.8	B-1	0.01
Example-7	A-1	2.0×10^{-5}	32	22	C-1	0.8	B-1	0.01
Example-8	A-1	1.0×10^{-5}	2	3	C-1	0.3	B-1	0.01
Example-9	A-1	1.0×10^{-5}	3	3	C-1	0.5	B-1	0.01
Example-10	A-1	1.0×10^{-5}	3	3	C-1	1	B-1	0.01
Example-11	A-1	1.0×10^{-5}	5	8	C-1	1.4	B-1	0.01
Example-12	A-1	1.0×10^{-5}	3	8	C-2	0.8	B-1	0.01
Example-13	A-1	1.0×10^{-5}	3	8	C-3	0.8	B-1	0.01
Example-14	A-1	1.0×10^{-5}	2	5	C-4	0.8	B-1	0.01
Example-15	A-1	1.0×10^{-5}	3	8	C-1	0.8	D-1	0.01
Example-16	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.01

	Poly- meriza- tion catalyst	Catalyst concen- tration (mol %)	Water in monomer (ppm)	Formic acid in monomer (ppm)	Comono- mer	Comono- mer amount (mol %)	Deacti- vating agent	Amount of deactivating agent added (phr)
Example-17	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.01
Example-18	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.01
Example-19	A-2	5.0×10^{-6}	2	5	C-1	0.8	B-1	0.01
Example-20	A-2	1.0×10^{-5}	17	25	C-1	1.4	B-1	0.01
Example-21	A-3	5.0×10^{-6}	2	8	C-1	0.8	B-1	0.01
Example-22	A-3	1.0×10^{-5}	28	5	C-1	0.3	B-1	0.01
Example-23	A-4	1.0×10^{-5}	5	8	C-1	0.8	B-1	0.01
Example-24	A-1	1.0×10^{-5}	3	8	C-1	0.3	B-1	0.01
Example-25	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.01
Example-26	A-1	1.0×10^{-5}	3	8	C-1	1.4	B-1	0.01
Example-27	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.005
Example-28	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.05

Table 1-1 (cont'd)

	Polymerization yield (%)	Formate terminal D_{1710}/D_{1470}	Inserted oxyalkylene unit amount (mol%)	Sequence (mol%)	
				n=1	n>2
Example-1	89	0.010	0.24	99.7	0.3
Example-2	88	0.011	0.25	99.8	0.6
Example-3	92	0.013	0.23	99.4	0.6
Example-4	90	0.018	0.23	99.5	0.5
Example-5	95	0.014	0.22	99.2	0.8
Example-6	93	0.020	0.23	99.4	0.6
Example-7	91	0.024	0.23	99.5	0.5
Example-8	95	0.013	0.08	100	-
Example-9	94	0.013	0.15	100	-
Example-10	93	0.013	0.31	98.5	1.5
Example-11	90	0.015	0.43	97.2	2.8
Example-12	93	0.014	0.26	==	==
Example-13	91	0.015	0.27	==	==
Example-14	91	0.015	0.27	==	==
Example-15	89	0.013	0.25	99.5	0.5
Example-16	89	0.013	0.25	99.4	0.6

	Polymerization yield (%)	Formate terminal D_{1710}/D_{1470}	Inserted oxyalkylene unit amount (mol%)	Sequence (mol%)	
				n=1	n>2
Example-17	94	0.015	0.23	99.7	0.3
Example-18	94	0.014	0.22	99.7	0.3
Example-19	88	0.012	0.23	99.5	0.5
Example-20	90	0.018	0.42	97.4	2.6
Example-21	86	0.014	0.22	99.6	0.4
Example-22	89	0.017	0.09	100	-
Example-23	92	0.015	0.23	99.5	0.5
Example-24	95	0.012	0.08	100	-
Example-25	94	0.012	0.22	99.6	0.4
Example-26	94	0.012	0.42	98.4	1.6
Example-27	==	==	==	==	==
Example-28	==	==	==	==	==

Table 1-2

	Poly- meriza- tion catalyst	Catalyst concen- tration (mol %)	Water in monomer (ppm)	Formic acid in monomer (ppm)	Comono- mer (mol %)	Deacti- vating agent	Amount of deactivating agent added (phr)
Example-29	A-1	1.0×10^{-5}	3	8	C-1	B-2	0.01
Example-30	A-1	1.0×10^{-5}	3	8	C-1	B-3	0.01
Example 31	A-1	1.0×10^{-5}	3	8	C-1	B-4	0.02
Comp. Example-1	A-5	5.0×10^{-3}	2	3	C-1	B-1	0.01
Comp. Example-2	A-5	2.0×10^{-3}	2	3	C-1	B-1	0.01
Comp. Example-3	A-5	1.0×10^{-3}	2	3	C-1	==	==
Comp. Example-4	A-5	1.0×10^{-3}	2	3	C-1	==	==
Comp. Example-5	A-5	2.0×10^{-3}	2	3	C-1	B-1	0.01
Comp. Example-6	A-5	2.0×10^{-3}	2	3	C-1	B-1	0.01
Comp. Example-7	A-5	2.0×10^{-3}	2	3	C-5	B-1	0.01
Comp. Example 8	A-5	2.0×10^{-3}	2	3	C-5	B-1	0.01

	Poly- meriza- tion catalyst	Catalyst concen- tration (mol %)	Water in monomer (ppm)	Formic acid in monomer (ppm)	Comono- mer	Comono- mer amount (mol %)	Deacti- vating agent	Amount of deactivating agent added (phr)
Comp. Example-9	A-5	2.0×10^{-3}	2	3	C-5	0.8	B-5	==
Comp. Example-10	A-5	2.0×10^{-3}	2	3	C-5	1.4	B-5	==
Comp. Example-11	A-1	1.0×10^{-6}	2	3	C-1	0.8	==	==
Comp. Example-12	A-1	2.0×10^{-5}	52	8	C-1	0.8		
Comp. Example-13	A-1	2.0×10^{-5}	2	55	C-1	0.8	==	==
Comp. Example-14	A-1	5.0×10^{-5}	52	8	C-1	0.8	B-1	0.05
Comp. Example-15	A-1	5.0×10^{-5}	2	55	C-1	0.8	==	==
Comp. Example-16	A-1	5.0×10^{-5}	2	3	C-1	0.8	B-1	0.01
Comp. Example-17	A-1	1.0×10^{-5}	2	3	C-1	0.18	B-1	0.01
Comp. Example-18	A-1	1.0×10^{-5}	2	3	C-1	0.1	B-1	0.01
Comp. Example-19	A-1	1.0×10^{-5}	2	3	C-1	2.2	B-1	0.01

	Poly- meriza- tion catalyst	Catalyst concen- tration (mol %)	Water in monomer (ppm)	Formic acid in monomer (ppm)	Comono- mer	Comono- mer amount (mol %)	Deacti- vating agent	Amount of deactivating agent added (phr)
Comp. Example-20	A-1	1.0×10^{-5}	2	3	C-1	3.5	B-1	0.01
Comp. Example-21	A-1	1.0×10^{-5}	3	8	C-1	0.3	B-1	0.01
Comp. Example-22	A-1	1.0×10^{-5}	3	8	C-1	0.3	B-1	0.05
Comp. Example-23	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.01
Comp. Example-24	A-1	1.0×10^{-5}	3	8	C-1	0.8	B-1	0.05
Comp. Example-25	A-1	1.0×10^{-5}	3	8	C-1	1.4	B-1	0.01

Table 1-2 (Cont'd)

	Polymerization yield (%)	Formate terminal D_{1710}/D_{1470}	Inserted oxyalkylene unit amount (mol%)	Sequence (mol%)	
				n=1	n>2
Example-29	==	==	==	==	==
Example-30	==	==	==	==	==
Example-31	==	==	==	==	==
Comp. Example 1	84	0.045	0.23	93.6	6.4
Comp. Example-2	72	0.041	0.25	94.3	5.7
Comp. Example-3	Non- polymerizable	==	==	==	==
Comp. Example-4	Non- polymerizable	==	==	==	==
Comp. Example-5	61	0.047	0.17	93.8	6.2
Comp. Example-6	55	0.042	0.44	94.1	5.9
Comp. Example-7	56	0.048	0.28	92.2	7.8
Comp. Example-8	52	0.047	0.45	90.8	9.2

	Polymerization yield (%)	Formate terminal D_{1710}/D_{1470}	Inserted oxyalkylene unit amount (mol%)	Sequence (mol%)	
				n=1	n>2
Comp. Example-9	70	0.040	0.28	93.2	6.8
Comp. Example-10	65	0.044	0.45	89.5	10.5
Comp. Example-11	Non- polymerizable	==	==	==	==
Comp. Example-12	42	==	==	==	==
Comp. Example-13	Non- polymerizable	==	==	==	==
Comp. Example-14	64	0.030	0.28	98.4	1.6
Comp. Example-15	39	==	==	==	==
Comp. Example-16	95	0.030	0.24	98.9	1.2
Comp. Example-17	92	0.013	0.05	100	-
Comp. Example-18	92	0.012	0.03	100	-
Comp. Example-19	90	0.015	0.62	97.8	3.2

	Polymerization yield (%)	Formate terminal D_{1710}/D_{1470}	Inserted oxyalkylene unit amount (mol%)	Sequence (mol%)	
				n=1	n>2
Comp. Example-20	90	0.018	1.02	96.8	4.2
Comp. Example-21	95	0.040	0.08	100	-
Comp. Example-22	95	0.040	0.08	100	-
Comp. Example-23	92	0.032	0.23	99.7	0.3
Comp. Example-24	92	0.032	0.23	99.7	0.3
Comp. Example-25	90	0.048	0.42	97.5	2.5

Table 2-1

	M.p. (°C)	MI (g/10 min)	Heat stability (min)	Tensile strength (kg/cm ²)
Example-1	172.2	10.6	101	712
Example-2	172.2	10.5	98	713
Example-3	172.5	9.2	90	715
Example-4	==	9.5	91	715
Example-5	172.8	8.8	86	715
Example-6	==	9.2	85	715
Example-7	==	9.5	85	715
Example-8	173.8	8.8	86	732
Example-9	173.1	9.0	87	725
Example-10	171.1	9.2	94	709
Example-11	170.2	10.6	103	702
Example-12	172.0	9.5	92	712
Example-13	171.8	9.2	90	712
Example-14	171.8	9.2	95	712
Example-15	172.1	45.2	90	712
Example-16	172.3	32.0	93	712
Example-17	172.5	3.2	96	715
Example-18	172.5	1.4	99	715
Example-19	172.4	9.0	96	715
Example-20	170.1	9.3	96	702
Example-21	162.5	8.8	97	715
Example-22	173.8	9.0	94	733
Example-23	==	9.5	91	715
Example-24	173.6	8.9	95	732
Example-25	172.5	9.2	100	715
Example-26	170.2	9.2	95	702
Example-27	==	9.2	91	715
Example-28	==	9.2	99	715

Table 2-1 (Cont'd)

	Heat aging resistance (%)			Hot water resistance (%)		
	500 hr	1,000 hr	2,000 hr	500 hr	1,000 hr	2,000 hr
Example-1	100	100	90	100	99	86
Example-2	100	100	92	100	98	85
Example-3	100	99	91	100	98	85
Example-4	100	97	90	100	97	84
Example-5	100	98	91	100	97	84
Example-6	100	97	88	100	95	85
Example-7	100	98	90	100	95	85
Example-8	100	96	88	100	96	83
Example-9	100	97	89	100	96	83
Example-10	100	99	94	100	98	87
Example-11	100	100	95	100	98	92
Example-12	100	99	90	100	98	86
Example-13	100	98	90	100	98	85
Example-14	100	98	89	100	99	86
Example-15	100	98	92	100	98	85
Example-16	100	98	92	100	98	85

	Heat aging resistance (%)			Hot water resistance (%)		
	500 hr	1,000 hr	2,000 hr	500 hr	1,000 hr	2,000 hr
Example-17	100	99	94	100	98	87
Example-18	100	99	94	100	98	87
Example-19	100	100	94	100	99	86
Example-20	100	98	92	100	98	84
Example-21	100	100	95	100	99	86
Example-22	100	99	92	100	98	85
Example-23	100	98	92	100	98	84
Example-24	100	97	90	100	98	86
Example-25	100	99	94	100	99	90
Example-26	100	100	95	100	100	92
Example-27	100	98	90	100	99	84
Example-28	100	97	89	100	99	92

Table 2-2

	M.p. (°C)	MI (g/10 min)	Heat stability (min)	Tensile strength (kg/cm ²)
Example-29	==	9.2	95	715
Example-30	==	9.2	93	715
Example-31	==	9.2	95	715
Comp. Example-1	172.6	9.8	48	717
Comp. Example-2	172.5	10.0	53	715
Comp. Example-3	==	==	==	==
Comp. Example-4	==	==	==	==
Comp. Example-5	173.0	11.0	41	720
Comp. Example-6	170.4	11.2	50	702
Comp. Example-7	172.2	10.8	44	715
Comp. Example-8	170.0	10.8	44	705
Comp. Example-9	172.2	10.8	35	715
Comp. Example-10	170.5	10.8	40	705
Comp. Example-11	==	==	==	==
Comp. Example-12	==	==	==	==
Comp. Example-13	==	==	==	==
Comp. Example-14	172.0		38	715
Comp. Example-15	==	==	==	==
Comp. Example-16	172.5		52	712

	M.p. (°C)	MI (g/10 min)	Heat stability (min)	Tensile strength (kg/cm ²)
Comp. Example-17	174.3	9.4	60	732
Comp. Example-18	174.5	9.5	55	735
Comp. Example-19	168.0	9.8	101	668
Comp. Example-20	165.0	9.5	101	647
Comp. Example-21	173.6	10.0	95	730
Comp. Example-22	173.6	10.0	104	730
Comp. Example-23	171.0	9.8	100	715
Comp. Example-24	171.0	9.8	98	715
Comp. Example-25	170.0	9.8	107	705

Table 2-2 (cont'd)

	Heat aging resistance			Hot water resistance		
	500 hr	1,000 hr	2,000 hr	500 hr	1,000 hr	2,000 hr
Example-29	100	98	92	100	99	86
Example-30	100	98	92	100	99	86
Example-31	100	97	90	100	99	88
Comp. Example-1	100	76	52	100	67	26
Comp. Example-2	100	75	48	100	60	Unmeasurable
Comp. Example-3	==	==	==	100	==	==
Comp. Example-4	==	==	==	100	==	==
Comp. Example-5	100	75	49	100	62	22
Comp. Example-6	100	77	50	100	62	25
Comp. Example-7	100	71	43	100	60	22
Comp. Example-8	100	70	45	100	62	27

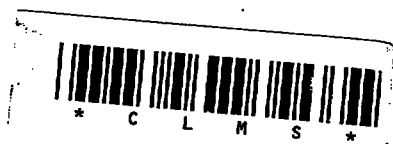
	Heat aging resistance				Hot water resistance		
	500 hr	1,000 hr	2,000 hr		500 hr	1,000 hr	2,000 hr
Comp. Example-9	100	67	Unmeasur- able		98	54	Unmeasur- able
Comp. Example-10	100	70	Unmeasur- able		99	58	Unmeasur- able
Comp. Example-11	==	==	==		==	==	==
Comp. Example-12	==	==	==		==	==	==
Comp. Example-13	==	==	==		==	==	==
Comp. Example-14	100	77	41		100	68	35
Comp. Example-15	==	==	==		==	==	==
Comp. Example-16	100	80	55		100	70	36
Comp. Example-17	100	85	62		100	78	52
Comp. Example-18	100	81	49		100	72	38
Comp. Example-19	==	==	==		==	==	==

	Heat aging resistance			Hot water resistance		
	500 hr	1,000 hr	2,000 hr	500 hr	1,000 hr	2,000 hr
Comp. Example-20	==	==	==	==	==	==
Comp. Example-21	100	77	50	100	65	23
Comp. Example-22	100	75	43	100	70	37
Comp. Example-23	100	81	55	100	70	35
Comp. Example-24	100	77	45	100	72	33
Comp. Example-25	100	74	40	100	66	27

1 INDUSTRIAL APPLICABILITY

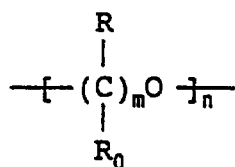
The copolymer of the present invention is excellent in strength, rigidity, fatigue characteristic, friction abrasion characteristic, heat stability, etc.

- 5 The copolymer can be put to various uses for which prior polyoxymethylene homopolymers and copolymers have been used, for example, mechanism elements such as cams, gears, switches, handles, levers, reels, hubs and bearings; miscellaneous goods such as fasteners, buttons
10 and clips; and further a large number of automotive, electric and electronic parts. Further, the copolymer can be used, by virtue of its excellent characteristics, for parts of water treatment, kitchen or toilet goods, such as pump impellers, pump casings, shower nozzles and
15 taps. The copolymer can also be formed into extruded rods or sheets, or blow-molded. It can be incorporated with known additives, for example, various antioxidants, heat stabilizers, pigments, nucleating agents, antistatic agents, weatherproofing agents, etc., and
20 various reinforcing materials, such as carbon fiber, glass fiber, glass beads, talc, mica, etc. Further, the copolymer can be made into polymer blends and polymer alloys with such polymers as polyurethane, PMMA, PE, etc.



CLAIMS

1. A polyoxymethylene copolymer having a molecular weight of 10,000-200,000 comprising oxymethylene units $(-\text{CH}_2\text{O})-$ and oxyalkylene units



wherein R and R_0 may be the same or different and are each selected from hydrogen, an alkyl group or an aryl group, n is 1 to 5, and m is 2 to 6, and wherein

(a) the proportion of oxyalkylene units to oxymethylene units is 0.07-0.5% by mole, and

(b) the ratio of the absorbance of terminal formate groups to methylene groups in the infrared spectrophotometry of the polymer is not more than 0.025.

2. The polyoxymethylene copolymer according to claim 1, wherein in the oxyalkylene units, the proportion of oxyalkylene units of $n=1$ is not less than 95% by mole of the whole oxyalkylene units.

3. The polyoxyalkylene copolymer according to claim 1 or 2, wherein the ratio of the absorbance of terminal formate groups to methylene groups in the infrared spectrophotometry of the polymer is not more than 0.020.

4. The polyoxymethylene copolymer according to claim 1 or 2 the terminal groups are each selected from

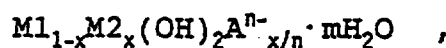


the group consisting of an alkoxy group, a hydroxyalkoxy group and a formate group.

5. A composition of the polyoxymethylene copolymer according to claim 1 or 2 which comprises, relative to 100 parts by weight of the polyoxymethylene copolymer, 0.001-0.5% by weight of at least one ion absorbent selected from

(a) ion adsorbents comprising as the main components at least two oxides selected from alkali metal oxides, alkaline earth metal oxides or oxides of trivalent or tetravalent elements, or

(b) ion adsorbents represented by the formula



wherein M1 denotes at least one divalent metal selected from alkaline earth metals, M2 denotes a trivalent metal, A^{n-} denotes an n-valent anion, x is a number satisfying $0 < x \leq 0.5$, and m is a positive number.

6. A process for producing a polyoxymethylene copolymer which comprises copolymerizing a mixture of a cyclic oligomer of formaldehyde or a cyclic acetal as the principal monomer with a comonomer copolymerizable therewith, in the presence of a perfluoroalkylsulfonic acid or a perfluoroalkylsulfonic acid derivative as the polymerization catalyst in an amount of 1×10^{-6} - 2×10^{-5} % by mole relative to the principal monomer, wherein the content of water and formic acid in the monomer mixture

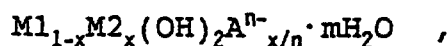


are, respectively, not more than 40 ppm by weight.

7. A process for producing a polyoxymethylene copolymer composition which comprises copolymerizing a mixture of a cyclic oligomer or cyclic acetal of formaldehyde as the principal monomer with a comonomer copolymerizable therewith, in the presence of a perfluoroalkylsulfonic acid or a perfluorosulfonic acid as the polymerization catalyst in an amount of 1×10^{-6} - 2×10^{-5} % by mole relative to the principal monomer, wherein the content of water and formic acid in the monomer mixture are, respectively, not more than 40 ppm by weight and deactivating the polymerization catalyst in the resulting polyoxymethylene copolymer, which comprises adding and melt-blending at least one ion adsorbent selected from

(a) ion adsorbents comprising as the main components at least two kinds of oxides selected from alkali metal oxides, alkaline earth metal oxides, and oxides of trivalent and tetravalent elements, or

(b) ion adsorbents represented by the formula



wherein M1 denotes at least one divalent metal selected from alkaline earth metals, M2 denotes a trivalent metal, A^{n-} denotes an n-valent anion, x satisfies $0 < x \leq 0.5$, and m is a positive number, in an amount of 0.001-0.5% by weight relative to the polymer to obtain



the polyoxymethylene copolymer composition.

ABSTRACT

POLYOXYMETHYLENE COPOLYMER AND PROCESS FOR
PRODUCING THE COPOLYMER

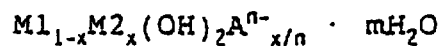
A polyoxymethylene copolymer excellent in stability and mechanical properties which is comprised of oxymethylene units and oxyalkylene units and has a molecular weight of 10,000 to 200,000. The proportion of oxyalkylene units to oxymethylene units is 0.07 to 0.5% by mole and the ratio of the absorbance of terminal formate groups to that of methylene groups determined by infrared spectrophotometry is not more than 0.025. A process for producing the copolymer is also disclosed.

1 not more than 100 minutes.

After polymerization, the catalyst is usually deactivated since the catalyst contained in the polymer produced causes depolymerization. The deactivation is
 5 generally conducted by contacting the polymer with an aqueous solution or an organic solvent containing a basic substance such as triethylamine or by adding and melt-blending a basic substance with the polymer to neutralize and deactivate the catalyst. The present
 10 inventors have made extensive study on the methods of deactivating the polymerization catalyst and resultantly found, as an utterly novel method, a highly effective method in which deactivation is conducted by adding and melt-blending with the copolymer a crystalline acidic
 15 adsorbent comprising at least two kinds of metal oxides or metal hydroxides. In more particular, ~~to 100 parts~~
~~by weight of~~ ^{the} polyoxymethylene copolymer, there is preferably added and melt-blended 0.001-0.5% by weight, more preferably 0.005-0.1% by weight, of at least one
 20 adsorbent selected from

a) ion adsorbents comprising at least two kinds of oxides selected from alkali metal oxides, alkaline earth metal oxides, and oxides of trivalent and tetravalent elements, or

25 b) ion adsorbents represented by the formula



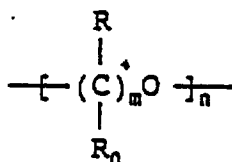
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CLAIMS

1. A polyoxymethylene copolymer having a molecular weight of 10,000-200,000 comprising oxymethylene units $(-\text{CH}_2\text{O})-$ and oxyalkylene units



wherein R and R_0 may be the same or different and are each selected from hydrogen, an alkyl group or an aryl group, n is 1 to 5, and m is 2 to 6, and wherein

(a) the proportion of oxyalkylene units to oxymethylene units is 0.07-0.5% by mole, and

(b) the ratio of the absorbance of terminal formate groups to methylene groups in the infrared spectrophotometry of the polymer is not more than 0.025.

2. The polyoxymethylene copolymer according to claim 1, wherein in the oxyalkylene units, the proportion of oxyalkylene units of $n=1$ is not less than 95% by mole of the whole oxyalkylene units.

3. The ~~polyoxyalkylene~~ ^{polyoxymethylene} copolymer according to claim 1 or 2, wherein the ratio of the absorbance of terminal formate groups to methylene groups in the infrared spectrophotometry of the polymer is not more than 0.020.

4. The polyoxymethylene copolymer according to claim 1 or 2 the terminal groups are each selected from

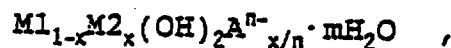


the group consisting of an alkoxy group, a hydroxyalkoxy group and a formate group.

5. A composition of the polyoxymethylene copolymer according to claim 1 or 2 which comprises, relative to ~~100 parts by weight of~~ the polyoxymethylene copolymer, 0.001-0.5% by weight of at least one ion adsorbent ~~absorbent~~ selected from

(a) ion adsorbents comprising as the main components at least two oxides selected from alkali metal oxides, alkaline earth metal oxides or oxides of trivalent or tetravalent elements, or

(b) ion adsorbents represented by the formula



wherein M1 denotes at least one divalent metal selected from alkaline earth metals, M2 denotes a trivalent metal, A^{n-} denotes an n-valent anion, x is a number satisfying $0 < x \leq 0.5$, and m is a positive number.

~~6. A process for producing a polyoxymethylene copolymer which comprises copolymerizing a mixture of a cyclic oligomer of formaldehyde or a cyclic acetal as the principal monomer with a comonomer copolymerizable therewith, in the presence of a perfluoroalkylsulfonic acid or a perfluoroalkylsulfonic acid derivative as the polymerization catalyst in an amount of 1×10^{-6} - 2×10^{-5} % by mole relative to the principal monomer, wherein the content of water and formic acid in the monomer mixture~~

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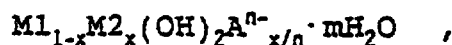


~~are, respectively, not more than 40 ppm by weight.~~

6. A process for producing a polyoxymethylene copolymer composition which comprises copolymerizing a mixture of a cyclic oligomer or cyclic acetal of formaldehyde as the principal monomer with a comonomer copolymerizable therewith, in the presence of a perfluoroalkylsulfonic acid or a perfluorosulfonic acid as the polymerization catalyst in an amount of 1×10^{-6} - 2×10^{-5} % by mole relative to the principal monomer, wherein the content of water and formic acid in the monomer mixture are, respectively, not more than 40 ppm by weight and deactivating the polymerization catalyst in the resulting polyoxymethylene copolymer, which comprises adding and melt-blending at least one ion adsorbent selected from

(a) ion adsorbents comprising as the main components at least two kinds of oxides selected from alkali metal oxides, alkaline earth metal oxides, and oxides of trivalent and tetravalent elements, or

(b) ion adsorbents represented by the formula



wherein M1 denotes at least one divalent metal selected from alkaline earth metals, M2 denotes a trivalent metal, A^{n-} denotes an n-valent anion, x satisfies $0 < x \leq 0.5$, and m is a positive number, in an amount of 0.001-0.5% by weight relative to the polymer to obtain

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the polyoxymethylene copolymer composition.

7. The polyoxymethylene copolymer according to claim 1 or 2,
wherein the proportion of oxyalkylene units to oxymethylene units is 0.1
to 0.3% by mole.
8. The composition according to claim 5, wherein the proportion
of oxyalkylene units to oxymethylene units in said polyoxymethylene copolymer
is 0.1 to 0.3% by mole.
9. The composition according to claim 5, wherein said ion adsorbent is
contained in an amount of 0.005 to 0.1% by weight, based on the weight of said
polyoxymethylene copolymer.
10. The process according to claim 7, wherein said ion adsorbent is
added in an amount of 0.005 to 0.1% by weight, based on the weight of said
polyoxymethylene copolymer.

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