

AMENDED

CONVENTION



AUSTRALIA

Patents Act

APPLICATION FOR A STANDARD PATENT

026321

I/We ATOCHEM NORTH AMERICA, INC.

of Pennwalt Building
Three Parkway
Philadelphia, Pennsylvania 19102
United States of America

hereby apply for the grant of a standard patent for an invention entitled:

PROCESS FOR PREPARING SULFUR SOLVENT COMPOSITIONS

which is described in the accompanying complete specification.

Details of basic application

Number of basic application: 255,221

Convention country in which
basic application was filed: UNITED STATES OF AMERICA

Date of basic application : 11 October, 1988

Address for Service:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

Dated: 15 April 1991

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
ATOACHEM NORTH AMERICA, INC.

By:

David B Fitzpatrick

Our Ref : 41375/89

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DECLARATION FOR A PATENT APPLICATION

▼ INSTRUCTIONS

- (a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) Convention application made by
(b) PENNWALT CORPORATION

- (c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(s)" for a patent (c) for an
invention entitled (d)
PROCESS FOR PREPARING SULFUR SOLVENT COMPOSITIONS

- (e) Insert FULL name(s) AND address(es) of declarant(s)
(See headnote*)

X/We (e) Madelyne R. Raksnis, Assistant Secretary, of
PENNWALT CORPORATION, Pennwalt Building, Three Parkway
Philadelphia, Pennsylvania 19102, UNITED STATES OF AMERICA

do solemnly and sincerely declare as follows:

1. ~~I am/We are the applicant(s).~~
(or, in the case of an application by a body corporate)
1. I am/We are authorized to make this declaration on behalf of the applicant(s).
2. ~~I am/We are the actual inventor(s) of the invention.~~
(or, where the applicant(s) is/are not the actual inventor(s))

- (f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f)
Glenn Thomas Carroll: 2437 Chestnut Avenue, Jeffersonville,
Pennsylvania 19403, United States of America
Michael Jeffrey Lindstrom: 425 Willow Circle, Downingtown,
Pennsylvania 19335, United States of America
is/are the actual inventor(s) of the invention and the facts upon which the applicant(s)
is/~~are~~ entitled to make the application are as follows:

- (g) Recite how applicant(s) derive(s) title from actual inventor(s)
(See headnote**)

- (g)
Applicant is the assignee of the inventors

(Note: Paragraphs 3 and 4 apply only to Convention applications)

- (h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based is/~~are~~ identified by country, filing date, and basic applicant(s) as follows:

- (h)
UNITED STATES OF AMERICA
11 October, 1988
Glenn Thomas Carroll
Michael Jeffrey Lindstrom

4. The basic application(s) referred to in paragraph 3 hereof was/~~were~~ the first application(s) made in a Convention country in respect of the invention the subject of the application.

- (k) Insert PLACE of signing

Declared at (k) Philadelphia, Pennsylvania
19102, U.S.A.

- (l) Insert DATE of signing

Dated (l) August 21, 1989

- (m) Signature(s) of declarant(s)

(m) Madelyne R. Raksnis
Madelyne R. Raksnis
Assistant Secretary
FOR AND ON BEHALF OF
PENNWALT CORPORATION

Note: No legalization or other witness required

To: The Commissioner of Patents

(12) PATENT ABRIDGMENT (11) Document No. AU-B-41375/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 626321

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PROCESS FOR PREPARING SULFUR SOLVENT COMPOSITIONS
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- (71) Applicant(s)
ATOCHEM NORTH AMERICA, INC.
- (72) Inventor(s)
GLENN THOMAS CARROLL; MICHAEL JEFFREY LINDSTROM
- (74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK, 367 Collins Street, MELBOURNE VIC 3000
- (56) Prior Art Documents
AU 602576 15384/88 C01B 17/20
- (57) Claim

1. A process for preparing a liquid sulfur-solvent composition containing a major proportion of a sulfide or mixture of sulfides having the formula RSS_aSR' where R and R' are independently alkyl, alkaryl, alkoxyalkyl or hydroxy-alkyl radicals having from 1 to 24 carbon atoms in the alkyl moieties, phenyl or C₁-C₂₀ alkyl substituted phenyl and the value of a is 0 to 3, and a catalyst for improving the ability of said composition to take up sulfur, said process comprising treating said composition, either before, during or after the addition of said catalyst to said composition, with a primary or secondary amine in an effective amount and for an effective period of time to inhibit the deleterious effects of impurities in such composition.

4. The process of claim 1 wherein said primary or secondary amine is a polyalkyleneoxyamine or polyamine.

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11. The process of claim 1 wherein said sulfide is
dimethyl disulfide, dimethyl polysulfide or mixture thereof.

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Class

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- 1 -

Process for Preparing Sulfur Solvent Compositions

(IR 2965)

BACKGROUND

This invention relates to a process for preparing
5 catalyst containing, sulfur-solvent compositions wherein such
compositions are treated, before, during or after
incorporation of said catalysts, to inhibit the deleterious
effects of impurities. More particularly, it relates to a
process wherein sulfide-containing, sulfur solvents are
10 treated with primary or secondary amines whereby the catalyst
poisoning effects of impurities in the solvent are inhibited.

In the processing of sour gas wells, sulfur may form deposits that can plug the well and terminate production. These deposits have been prevented or minimized by flowing solvents such as carbon disulfide, organic solvents, and aqueous alkylamines (U.S. 3,545,916), downhole. The solvent is injected and the well is allowed to soak for a sufficient period of time to dissolve any existing sulfur plugs. Alternatively, the solvent can be injected continuously in amounts sufficient to prevent the formation of sulfur deposits.

Dialkyl disulfides, either alone or blended with dialkyl sulfides (U.S. 3,531,160), have become the sulfur solvents of choice. Hyne [Alberta Sulfur Research Ltd. (ASRL), Quarterly Bulletin, vol. XVIII, Nos. 2, 3, and 4, 1982, p. 44] has shown that lower dialkyl disulfides, especially dimethyl disulfide (DMDS) are preferred. Alone they take up only a limited amount of sulfur; however, in conjunction with a suitable catalyst system, they will take up approximately 1.5 times their weight in sulfur at room temperature.

Impurities which may occur in the sulfide-catalyst compositions referred to above will poison the catalyst and prevent it from improving the ability of the composition to take up or dissolve sulfur. These impurities, including carbon disulfide and alkyl mercaptans, are formed within the dialkyl disulfide or polysulfide during manufacture. In addition, when these compositions are injected into a

sour gas well they are exposed to impurities from the well gas stream which impurities, including carbon disulfide and carbon oxysulfide, are increased as the bottom-hole temperature and pressure increase (Hyne, J.B. et al.,
5 World Oil, 1980, October, 111). In wells which contain high amounts of carbon disulfide and carbon oxysulfide, the catalyst in the sulfide composition may react with these impurities and become poisoned.

Prior Art

10 It is known to circulate liquid alkyl sulfides or disulfides in a sour gas well to dissolve and remove sulfur (U.S. 3,531,160). It is also known to catalyze a liquid (di)alkyl disulfide with various active compounds to substantially increase the sulfur take-up or solvent power of
15 the sulfide chemical. The use of a saturated aliphatic amine as a catalyst for the liquid dialkyl disulfide has been found very effective particularly subsequent to aging the sulfide-catalyst composition (U.S. 3,846,311).

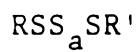
STATEMENT OF THE INVENTION

20 This invention is a process for preparing a liquid sulfur-solvent composition containing a major proportion of a sulfide or mixture of sulfides of the formula: RSS_aSR' where R and R' are independently alkyl, alkaryl, alkoxyalkyl or hydroxyalkyl radicals having from 1 to 24 carbon atoms in

the alkyl moieties, phenyl or alkyl substituted phenyl and the value of $\underline{a}$ is 0 to 3, and a catalyst for improving the ability of said composition to take up sulfur, said process comprising treating said composition, before, during or after
5 the addition of said catalyst to said composition, with a primary or secondary amine in an effective amount and for an effective period of time.

Detailed Description of the Invention

The liquid sulfur-solvent compositions of this
10 invention will contain a major proportion of a sulfide (or mixture thereof) having the formula



where R and R' are independently alkyl, alkaryl, alkoxyalkyl or hydroxyalkyl radicals having from 1 to 24, preferably
15 from 1 to 8 carbon atoms in the alkyl moiety, phenyl or C₁-C₂₀ alkyl substituted phenyl. Examples of these substituents include, methyl, ethyl, propyl, butyl, isobutyl, hexyl, octyl, isooctyl, decyl, dodecyl, octadecyl, phenyl, tolyl, xylyl and the like.

20 The value of $\underline{a}$ in the above formula is from 0 to 3 and, in a mixture of such sulfides, represents the average number of internal sulfurs and not the maximum number of sulfurs for any one species in the mixture.

The catalysts for the sulfur-solvent composition
25 include the catalysts mentioned in the prior art as useful

for improving the sulfur uptake capacity of the sulfide and
those disclosed in ^{Australian Patent Nos. 602,576 and 607,215} ~~depending, coassigned applications SN~~

~~047,956 and SN 047,955 filed on May 8, 1987~~ and claiming,

respectively, the use of polyalkyleneoxyamines or poly-amines
5 and a mixture of a basic nitrogen-containing compound with an
alcoholic or aqueous solution of an alkali hydroxide, alkoxide
or carbonate. Examples of catalysts disclosed in the prior
art are the unsubstituted, saturated amines, fatty acid
amines, sodium hydrosulfide-dimethyl-formamide cosolvent,
10 alkali salts of thiophenols-dimethyl-formamide cosolvent.

Example of catalysts of the afore-mentioned depending appli-
cations are combinations of basic nitrogen-containing
compounds including, for example, ammonia, aliphatic amines,
aryl amines, alkaryl amines, poly(alkyleneoxy)alkanolamines
15 and their respective ethers, polyalkyleneoxyamines and
polyamines, amides, sulfenamides, imines, and enamines, and
alcoholic or aqueous solution of alkali hydroxide or alkoxide,
for example, sodium or potassium hydroxide or alkoxide. The
catalyst of the depending applications include polyalkylene-
20 oxyamines and polyamines containing a primary or secondary
amine functionality and wherein the alkylene radical is a
substituted or unsubstituted radical having 2 to 4 carbon
atoms exclusive of substituent groups. Further examples

of these amines are identified under formulas 1, 2, 3 and

^{Australian Patent Nos. 607,215 and 602,576}
25 4 of ~~depending applications SN 049,955 and SN 049,956 filed~~

~~May 8, 1987~~

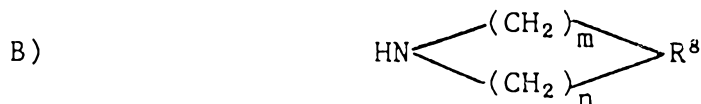


The catalysts of the process of this invention are used in the herein described sulfide-catalyst compositions in amounts ranging from 0.05% up to about 10% based on the weight of the composition.

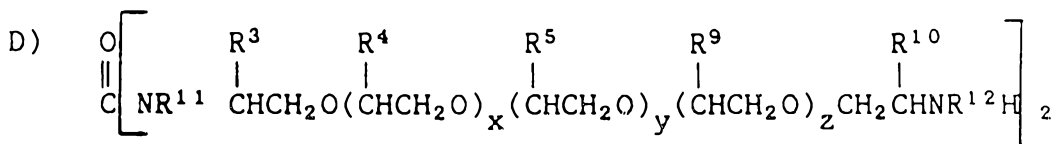
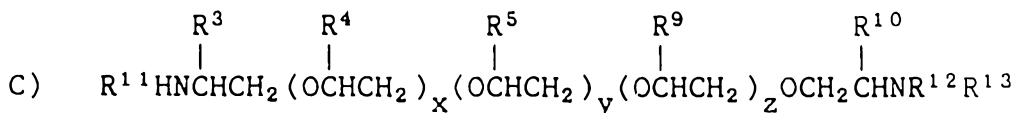
5 Examples of the amines which will inhibit the catalyst poisoning capability of impurities in the composition include compounds of the formulae:



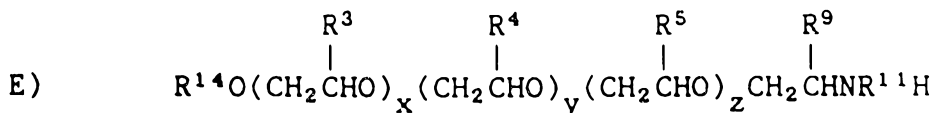
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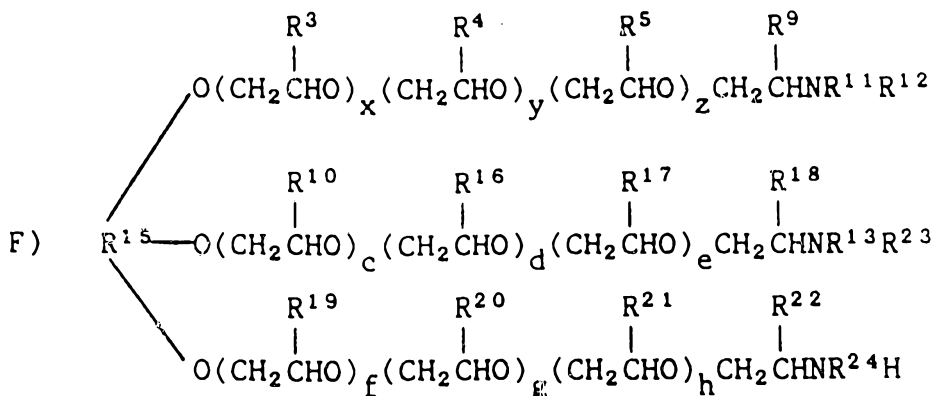
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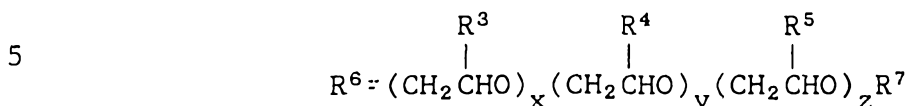
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where R¹ and R² are independently H, alkyl, alkaryl, hydroxy-alkyl, alkoxyalkyl wherein the alkyl moieties have from 1 to 20, preferably 1 to 6 carbon atoms, aryl or R⁶ where

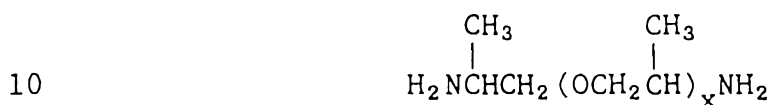


and R³, R⁴, R⁵, R⁷, R⁹, R¹⁰, R¹⁴, R¹⁶, R¹⁷, R¹⁸, R¹⁹, R²⁰, R²¹, and R²² are independently H, alkyl, alkaryl, hydroxy-alkyl, alkoxyalkyl, haloalkyl wherein the alkyl moieties have from 1 to 20, preferably 1 to 6 carbon atoms, or phenyl; R⁸ is CH₂, O, S, or NR¹; R¹¹, R¹², R¹³, R²³, and R²⁴ are independently H, alkyl and alkaryl wherein the alkyl moieties have from 1 to 10 carbon atoms, aryl, or CONH₂; R¹⁵ is the hydrocarbon residue of a triol; m and n are independently integers of from 1 to 6, and c, d, e, f, g, h, x, y, and z are independently integers of from 0-200 provided, however, that the total of such integers equal at least 2.

Formulas A-F, shown above, are given as examples of the primary or secondary amines useful as inhibitors of sulfide impurities for this invention. Any compound having a primary or secondary amine functionality, including those disclosed above as catalysts, are effective.

The preferred primary (p-) or secondary (sec-) amines used for the treatment procedure of this invention include the alkylamines and alkanolamines represented by the above formula A. More preferably, the p- and sec- amines are alkyl and alkanolamines having from 1 to 6 carbon atoms in

the alkyl moieties; most preferably, ethylamine or ethanol-
amine are used. Also included as preferred p- or sec-
amines are the polyalkyleneoxyamines or polyamines repre-
sented by the previously described formulae A where R¹ and
5 R² = R⁶, C, D, E, and F, particularly Jeffamine® D230,
a polyalkyleneoxypolyamine sold by Texaco Chemical Company
and having the formula:



where x is 2.6.

The amounts of the p- or sec- amines used to inhibit
deleterious effects of impurities will depend on the
concentration of such impurities in the composition.
15 Accordingly, the p- or sec- amines will be used in amounts
sufficient to inhibit the catalyst poisoning effects of
impurities in the compositions. Amounts of 0.05% and less,
based on the sulfide in the composition are useful. However,
the preferred amounts will range from about 0.1 to 10% based
20 on the weight of the sulfide in the composition, most
preferably, from 0.1 to about 1 %.

The sulfide is treated with the amine for a period of
time, at the temperature employed, sufficient to inhibit the
deleterious effects of impurities in the sulfide. Generally,
25 from a few minutes to many hours will be useful treatment
periods. Preferably, the sulfide is treated with the amine

for a time period ranging from about 20 minutes to about 72 hours.

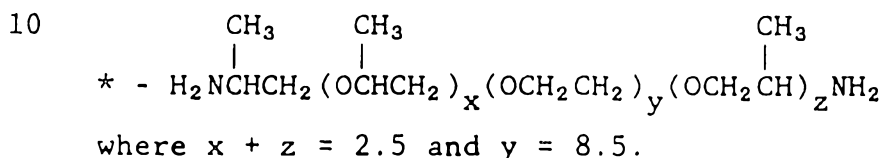
The temperature at which the sulfide is treated with the amine for any specified period of time is that
5 sufficient to inhibit the deleterious effects of impurities in the sulfide. The temperature will range from room temperature and below up to just below the boiling point of the composition. Preferably, the treatment temperature ranges from about 25° to about 80°C applied within the
10 preferred time period stated above.

The p- or sec-amine is used to treat the sulfur-solvent composition either before, during or after the addition of the catalyst system but preferably before. When utilizing catalyst compositions which are p- or sec-amines, an
15 additional amount of such catalyst, sufficient to overcome the deleterious effects of the impurities in the sulfide, may be added to the catalytic amount of such catalyst composition and the combined amount added to the sulfide. It is more economical, however, to first treat the sulfide with an
20 inexpensive amine to counter the deleterious effects of the impurities followed by the addition of a generally more expensive catalyst system.

The following examples are set forth to demonstrate this invention.

Example 1

A composition of 9.5 g of dimethyl disulfide, which contained approximately 0.5% carbon disulfide and 0.05% methyl mercaptan as determined by vapor phase chromatography, 5 60 microliters (μ l) Jeffamine[®] ED-600* and 6.5 μ l of dimethylaminoethanol was allowed to stand at room temperature for 4 hours. The composition was then bubbled with H₂S for 3 minutes, whereupon 3.5 g of sulfur were added. A time of 6.08 minutes was noted for the dissolution of the sulfur.



Example 2

15 A composition identical to that in Example 1, except that the dimethyl disulfide was treated with 0.1 wt% ethanolamine and allowed to stir for 25 minutes prior to the addition of the Jeffamine[®] ED-600 and the dimethyl- aminoethanol, was bubbled with H₂S for 3 minutes after the 20 composition stood for approximately 16 hours at room temperature. Sulfur (3.5 g) was then added and a time of 0.7 minutes was noted for its dissolution, thereby showing the effectiveness of said amine treatment process. Since the deactivation of the composition is caused by a reaction 25 between the impurity and the catalyst, Jeffamine[®] ED-600,

the composition was allowed to set for 16 hours instead of four to further show the effectiveness of the disclosed treatment process.

Example 3

5 A composition of 9.5 g of dimethyl disulfide, which contained no carbon disulfide and methyl mercaptan as determined by vapor phase chromatography and 40 μ l Jeffamine[®] ED-600 was bubbled with H₂S for 3 minutes, whereupon 3.5 g of sulfur were added. A time period of 0.68
10 minutes was noted for the dissolution of the sulfur showing that the decreased time in Example 2 was not caused simply by the addition of extra amine. Additionally, a lesser amount of catalyst, Jeffamine[®] ED-600, and dimethyl-aminoethanol, were used, thereby providing additional proof that the lower
15 time periods were not caused by adding additional amine.

~~CLAIMS~~ THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for preparing a liquid sulfur-solvent composition containing a major proportion of a sulfide or mixture of sulfides having the formula RSS_aSR' where R and
5 R' are independently alkyl, alkaryl, alkoxyalkyl or hydroxy-alkyl radicals having from 1 to 24 carbon atoms in the alkyl moieties, phenyl or C_1 - C_{20} alkyl substituted phenyl and the value of a is 0 to 3, and a catalyst for improving the
10 ability of said composition to take up sulfur, said process comprising treating said composition, either before, during or after the addition of said catalyst to said composition, with a primary or secondary amine in an effective amount and for an effective period of time to inhibit the deleterious effects of impurities in such composition.
- 15 2. The process of claim 1 wherein the catalyst is a polyalkyleneoxyamine or polyamine.
3. The process of claim 1 wherein said primary or secondary amine is an alkylamine or alkanolamine having alkyl moieties of from 1 to 20 carbon atoms.
- 20 4. The process of claim 1 wherein said primary or secondary amine is a polyalkyleneoxyamine or polyamine.

5. The process of claim 2 wherein said primary or secondary amine is an alkylamine or alkanolamine having alkyl moieties of from 1 to 6 carbon atoms.

6. The process of claim 2 wherein said primary or secondary
5 amine is a polyalkyleneoxyamine or polyamine.

7. The process of claim 1 wherein said composition is treated with said primary or secondary amine for a period of time ranging from 20 minutes to about 72 hours.

8. The process of claim 1 wherein the composition is
10 treated at a temperature of from about 25 to about 80°C.

9. The process of claim 1 wherein said composition is treated with said primary or secondary amine before the addition of said catalyst.

10. The process of claim 1 wherein the amount of primary
15 or secondary amine ranges from 0.1 to 10% based on the weight of the sulfide in said composition.

11. The process of claim 1 wherein said sulfide is dimethyl disulfide, dimethyl polysulfide or mixture thereof.

12. The process of claim 11 wherein said catalyst is a polyalkyleneoxyamine or polyamine.

13. The process of claim 12 wherein said primary or secondary amine is ethylamine or ethanolamine.

5 14. The process of claim 13 wherein said ethylamine or ethanolamine is used to treat the composition in an amount ranging from 0.1 to about 1%, based on the weight of the sulfide in the composition, and the temperature at which said composition is treated ranges from about 25 to about
10 80°C.

15 15. The process of claim 12 wherein said polyalkyleneoxyamine or polyamine is used to treat the composition in an amount ranging from 0.1 to about 1% based on the weight of the sulfide in the composition, and the temperature at which said composition is treated ranges from about 25 to about 80°C.

DATED: 13 September 1989

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:

~~PENNWALT CORPORATION~~
ATOCHEM NORTH AMERICA, INC.



16. A process according to claim 1 substantially as
hereinbefore described with reference to any one of examples 1
to 3.

5

DATED: 4 May 1992

PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

10 ATOCHEM NORTH AMERICA, INC.

David B Fitzpatrick

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