# DEVELOPMENT OF TECHNOLOGY FOR OBTAINING CORROSION INHIBITORS DURING ABSORPTION PURIFICATION OF GASES FROM ACIDIC COMPOUNDS

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**Annotatsiya.** Ushbu maqolada gazlarni absorbsion tozalash jarayonida vujudga keladigan kislotali birikmalar korroziyaga qarshi ingibitor olish texnologiyasini ishlab chiqish mavzusining bayoni keltirilgan bo'lib, unda tarkibida azot, fosfor va oltingugurt birikmalari mavjud bo'lgan yangi tarkibli korroziya ingibitorining sintezi va uni ishlab chiqarish texnologiyasi bo'yicha ma'lumotlar keltirilgan.

**Kalit so'zlari:** korroziya, ingibitor, absorber, absorbent, TFO (teosemikarbazid, ortofosfat va formali asosida sintez qilingan ingibitor), nordon komponentlar, oligomer, qovushqoqlik.

**Аннотация.** В данной статье представлено описание темы разработки технологии получения ингибиторов коррозии из кислых соединений, образующихся при абсорбционной очистке газов, а также описаны синтез и технология получения нового ингибитора коррозии, содержащего соединения азота, фосфора и серы. 'информация предоставил.

**Ключевые слова:** коррозия, ингибитор, поглотитель, абсорбент, ТФО (ингибитор, синтезированный на основе теосемикарбазида, ортофосфата и муравьиной кислоты), кислотные компоненты, олигомер, вязкость.

**Abstract.** In order to reduce the consequences of corrosion in gas processing industrial facilities, new methods and technologies for the synthesis of inhibitors are being studied, and in order to ensure compliance with environmental requirements, research is being conducted to obtain inhibitors and their compositions of various compositions. In this regard, special attention is paid to the creation of inhibitors and anti-corrosion coatings with high technical characteristics that prevent metal corrosion, using existing raw materials.

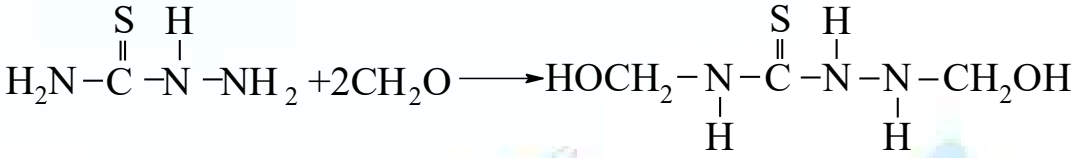
**Keywords:** corrosion, inhibitor, absorber, absorbent, TFO (inhibitor synthesized based on theosemicarbazide, orthophosphate and formic acid), acidic components, oligomer, viscosity.

**Introduction.** Taking this into account, based on the analysis of the obvious inhibitory properties of compounds containing sulfur, nitrogen and phosphorus containing electron pairs, formaldehyde and thiosemicarbazide were first mixed in certain proportions until a resinous appearance was obtained.

**Research methodology**. In this case, thiosemicarbazide first forms a resin in the form of monomethylol with formaldehyde. If formaldehyde is added in large quantities, a resin in the form of dimethylol is formed:

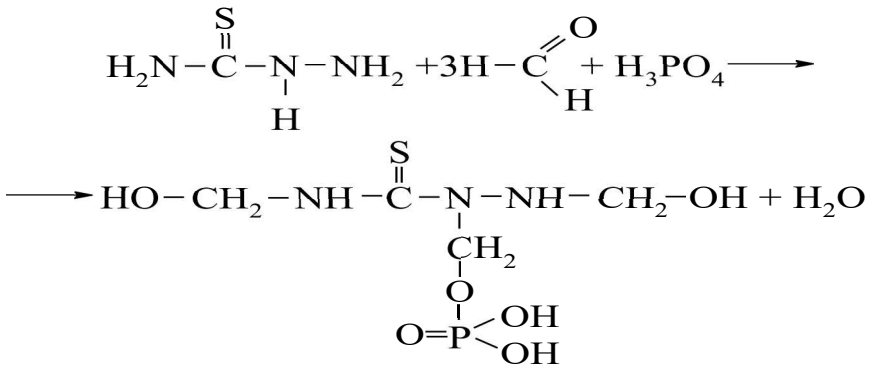


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As a result of the research, the ratio of reacting reagents in the copolycondensation of thiosemicarbazide, along with such parameters as reaction duration and temperature, was studied. According to the results obtained, the effect on the molecular weight of the oligomer was analyzed.

To get an idea of the linearity, branching, spatial structure and particle size of the synthesized inhibitor, their viscosities were studied. It was found that the substances react according to the following scheme:



The properties of thiosemicarbazide and formaldehyde resins, in particular their stability, can be improved by introducing some homologous aldehyde analogues into the oligomers.

The initial proportions of the reagents by mass were as follows: thiosemicarbazide (99.8%) 100 g, formalin (99.4%) 40-50 g, orthophosphoric acid (98.2%) 10 g, and water - 300 g.

The synthesis of a new corrosion inhibitor based on thiosemicarbazide, formalin, and orthophosphate compounds was carried out in the following laboratory apparatus (Figure 1).

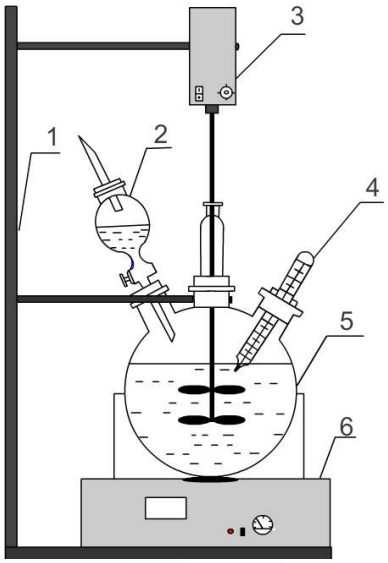



**Figure 1. Laboratory apparatus for obtaining TFO corrosion inhibitor**

1-stand; 2-product inlet; 3-reactor; 4-thermometer; 5-flask; 6-heater

A reactor with a height of 350 mm and a diameter of 40 mm was selected to carry out the synthesis process. Formalin and thiosemicarbazide



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were placed in a three-necked flask in a 3:1 molar ratio, placed in an oil bath, and mixed at a temperature of 20-30 °C for 7-10 minutes. In this case, thiosemicarbazide forms a resin in the form of dimethylol with formalin. The resin and orthophosphoric acid were mixed in a 4:1 molar ratio, and the temperature of the mixture was not allowed to rise above 60-65 °C. Orthophosphoric acid, as a modifier, chemically binds to the oligomer, increasing its solubility in water.

When the synthesis process is carried out for 0.3-0.5 hours, the resulting polycondensation product is light to dark brown in color, with a density of 1.22-1.35 g/cm$^3$ and pH=7.5-8.5. In variants I-II of the experiment, viscous oligomers were formed, and in variants III-IV, viscous-flowable oligomers were formed. This indicates that a product with a different physical state was formed as a result of the condensation between the oligomer and phosphoric acid. Modified oligomers are substances that are well soluble in water and ethanol. For comparison, thiosemicarbazide-formaldehyde oligomers were synthesized under the same conditions and their properties were studied. Table 1 shows the initial components and variants of the components for the preparation of the obtained oligomers.

***Table 1***

**Compositions and variants of starting components in the synthesis of oligomers**

| Names of components, amount of the main substance, in % | Test options and component consumption | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | I | | II | | III | | IV | |
| | heavy dark | Mass.% | heavy dark | Mass.% | heavy dark | Mass.% | heavy dark | Mass.% |
| Thiosemicarbazide- 99.8 | 100 | 22,2 | 100 | 22,7 | 100 | 20,4 | 100 | 20,4 |
| formaldehyde - 99,4 | 50 | 11,1 | 40 | 9,1 | 50 | 10,2 | 40 | 8,2 |
| Orthophosphoric acid – 98,2 | – | – | – | – | 40 | 8,2 | 50 | 10,2 |
| Water | 300 | 66,7 | 300 | 68,2 | 300 | 61,2 | 300 | 61,2 |
| Total | 450 | 100 | 440 | 100 | 490 | 100 | 490 | 100 |

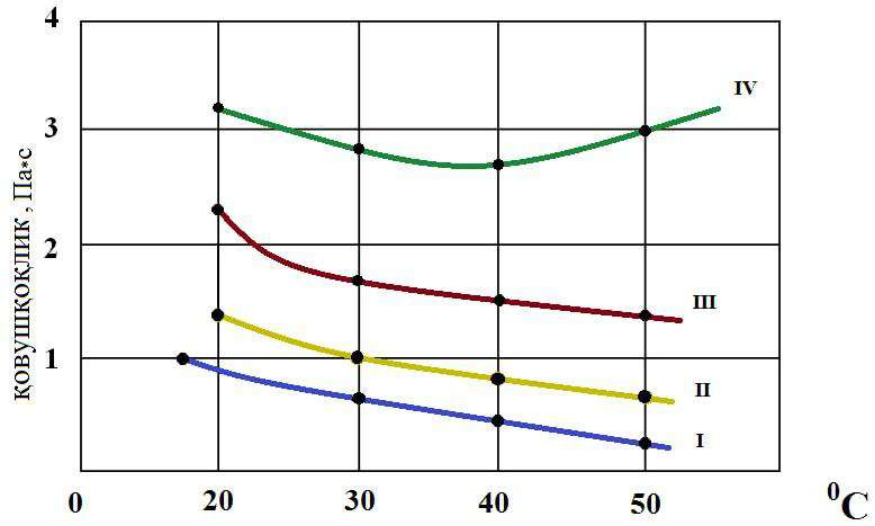
To date, the reaction mechanism for the formation of thiosemicarbazide-formaldehyde oligomers has not been fully studied, and based on existing mechanisms, a reaction mechanism scheme for the formation of methylol



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compounds with thiosemicarbazide, formaldehyde, and orthophosphoric acid modified with orthophosphoric acid for test variants I-IV was presented above.

The viscosity of the oligomers was measured on a HAAKE Viscotester 2 plus viscometer. The studies were carried out at temperatures of 20, 30, 40 and 50 °C. The viscosity values of the synthesized oligomers at different temperatures are presented in Figures 1




.

**Figure 3.2. Variation of oligomer viscosities at different temperatures for test samples I-IV.**

As can be seen from Figure1, the amount of acid introduced into the polycondensation reaction had a significant effect on the viscosity of the resulting oligomers. With increasing phosphoric acid consumption, the viscosity of the oligomers increases.

***Table 2***

**Molecular masses of the synthesized substances**

| Substance | Molecular mass g/mol | Gross formula (elemental composition) |
|---|---|---|
| Monomethylolthiosemicarbazide | 121 | $C_2H_7SN_3O$ |
| Dimethylolthiosemicarbazide | 151 | $C_3H_9SN_3O_2$ |
| Modified with orthophosphate acid | 278 | $C_4H_{13}SN_3O_7P$ |

The IR-spectral method allows for more reliable determination of the chemical structure of substances, including polymers. The structure of modified



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oligomers was determined using IR spectroscopy on a SHIMADZU device. The method of powdering substances in potassium bromide tablets was used for the samples (Figure 3)

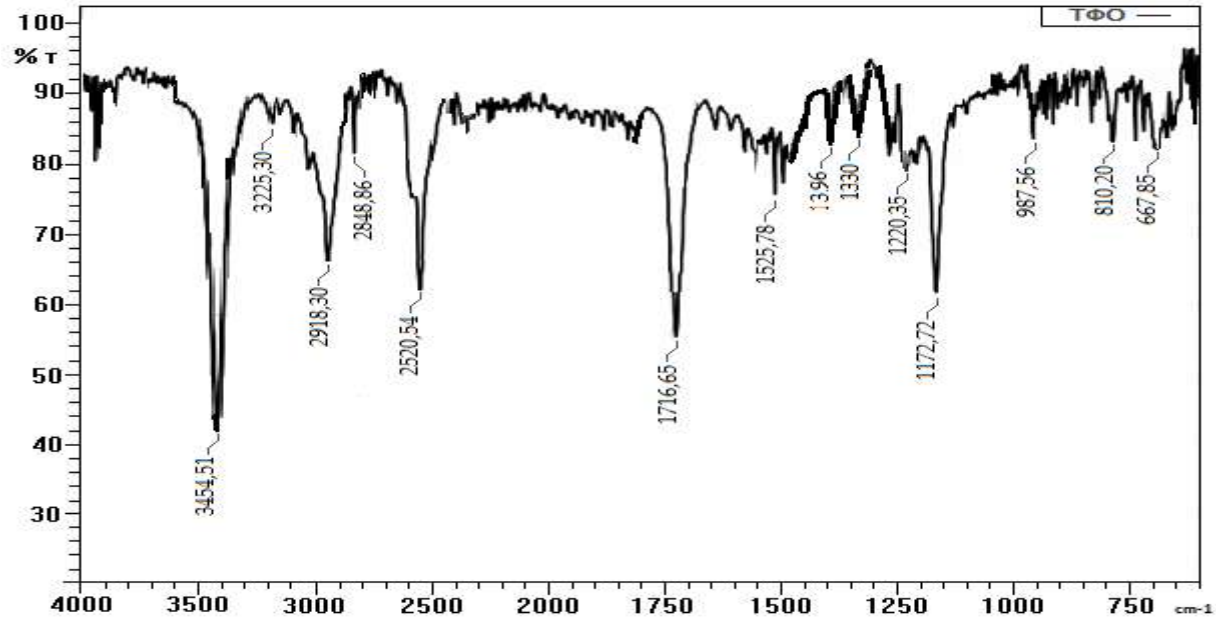



**Figure 3. IR spectrum of the modified oligomer**

In the IR spectrum, a line indicating the presence of the P=O group was observed in the 1172 $cm^{-1}$ region. In the 1396 $cm^{-1}$ region, a line indicating the presence of the–$CH_2$ group was observed. The highest absorption in the IR spectrum is observed in the 1716 $cm^{-1}$ region. It corresponds to the valence vibrations of the C=C double bond. Since this group is included in all starting materials, complete absorption occurs in this region.

It should be noted that for all samples, the absorption frequency of the –$CH_2$–NH– group is manifested in the 3300-3500 $cm^{-1}$ region with a decrease in intensity. The decrease in intensity can be explained by its participation in the formation of hydrogen bonds.

The IR spectrum of the synthesized compound contains lines in the region of 3454 $cm^{-1}$ belonging to the –CS–NH– group. Free hydroxyl groups and bound SO– groups are characterized by lines in the IR spectrum in the regions of 1525, 1396, 1330 $cm^{-1}$, respectively.

Analysis of the obtained IR spectra shows that the modifying and structuring effect of orthophosphoric acid included in the oligomers is confirmed. Thus, the obtained oligomer modified with orthophosphoric acid is not just a mechanical mixture of thiosemicabazide, formaldehyde, orthophosphoric acids, but an organic complex compound.



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Since the synthesized oligomer is soluble only in organic solvents, it was used after grinding to a dispersed state in a mill. A composition was developed to obtain a corrosion inhibitor.

In the production of oligomer resins, complete prevention of the formation of methylene groups is of particular importance. The reaction is carried out in a neutral (or weakly alkaline) medium at pH=7-8, and at the end in an acidic medium (pH=3-6.5). In order to make oligomer resins soluble in organic solvents, ensure good permeability of glues and enamels, and increase their resistance to water, their partial etherification with alcohols is carried out.

In practice, 40-70 % aqueous solutions or powders of oligomers are mainly used. The technology for producing these oligomers directly depends on the intended use of the oligomer.

The difference in the technological processes developed by us is mainly due to factors such as changes in the pH of the medium, the amount of orthophosphoric acid, temperature, process duration, and the ratio of reagents.

The technology includes the following steps:

1) mixing formalin and thiosemicarbazide in a certain ratio;

2) homogenizing the mixture for 30 minutes;

3) adding orthophosphoric acid to the reaction mixture and continuing condensation until the dynamic viscosity reaches 3.5-3.8 mPa*s;

4) achieving a pH value of 5.5 - 6.8.

Research has shown that the inhibitor should contain 300 g/l of thiosemicarbazide and 175-200 g/l of formaldehyde. This will produce a clear, syrupy, formaldehyde-free mass that is miscible with water in any ratio. Modification of the oligomer is carried out with orthophosphoric acid. The product yield is 86-88%.

Based on the results of the research, a technology for obtaining oligomers and their subsequent production was developed.

To obtain a modified oligomer, thiosemicarbazide, formalin solutions and orthophosphoric acids are used.

The thiosemicarbazide solution is a poorly soluble, flammable colorless crystalline powder in water, with a molar mass of 91.13 g/mol, a density of 1.376 g/cm$^3$, and a high viscosity solution, so it is collected by screw pump 1 into capacity 4 with a volume of 2m$^3$ (Figure 4).

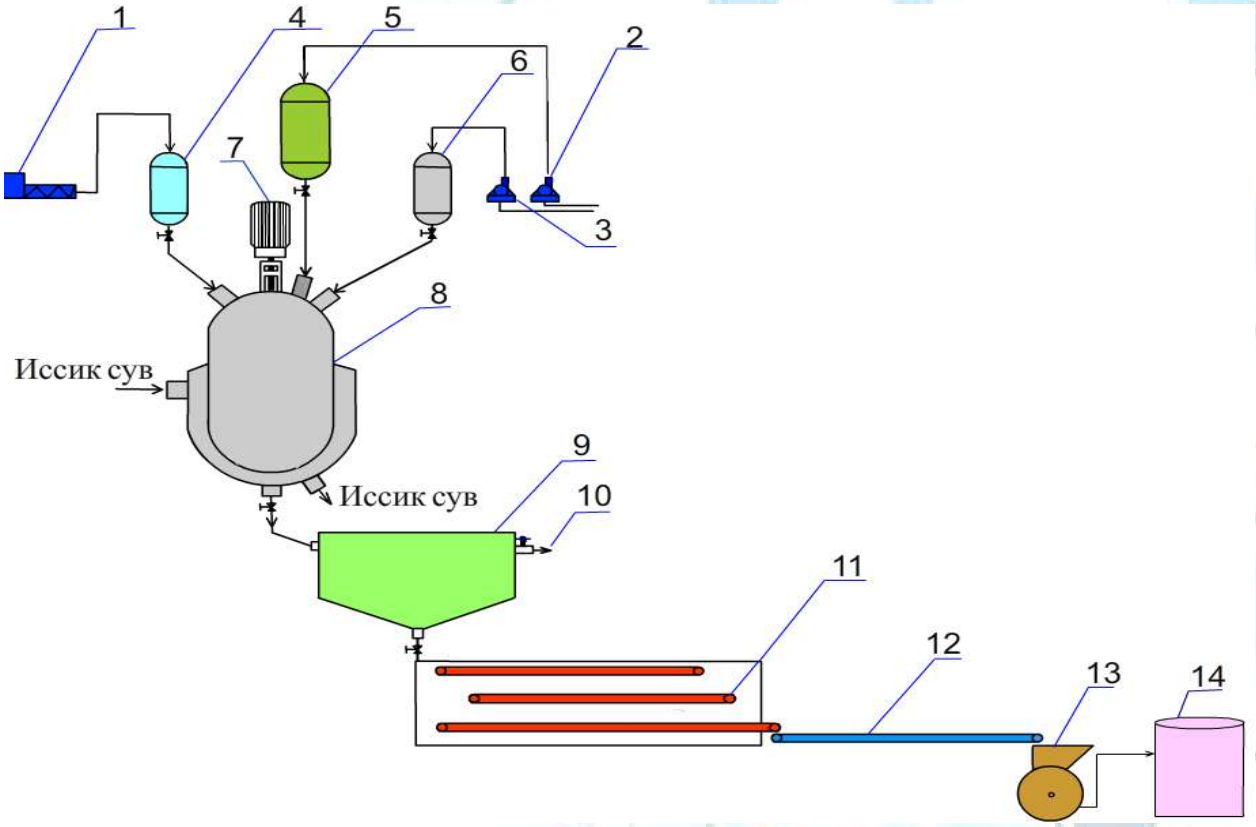
The formalin solution is an aqueous mixture stabilized with methanol, with a density of 1.1 g/cm$^3$, and is collected by centrifugal pump 2 into capacity 5. A



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capacity of 3m$^3$ made of corrosion-resistant metal is used to collect these components.

Orthophosphoric acid is an inorganic medium-strong acid with a molar mass of 98.0 g/mol and a density of 1.685 g/cm$^3$. This acid is transferred to the 6th tank installed in the system via a special centrifugal pump 3. A corrosion-resistant tank with a volume of 2 m$^3$ is used.




**4 - Figure. Technological scheme of the process of obtaining corrosion inhibitors from natural gas cleaning**

1-screw pump; 2,3-centrifugal pump; 4-dosing tank for thiosemicarbazide; 5-dosing tank for formalin; 6-dosing tank for orthophosphoric acid; 7-engine; 8-mixing reactor; 9-sedimentation device; 10-valve; 11-belt dryer; 12-belt conveyor; 13-grinding device; 14-storage tank.

The collected substances are transferred to a steam-jacketed reactor 8 equipped with a stirring device designed to heat the mixture to a temperature of 100 °C, type EMK R-1000. The reactor shaft consists of two blades and is controlled by a speed control unit. An AIR90L2 electric motor 7 is installed in the reactor. The electric motor has a power of 3 kW and a speed of 3000 rpm. Due to the high speed of movement, a reducer is installed. The speed of rotation on the reducer shaft is 90-100 rpm. The solutions are transferred from tanks 4 and 5 to the reactor and mixed for 10 minutes. Then, the orthophosphoric acid collected in tank 6 is transferred to


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a mixture of thiosemicarbazide and formalin formed as a result of processing in the reactor tank. The three components are processed in the reactor for 25 - 30 minutes with the heating agent steam (weak steam) at a temperature of 70 - 75 ºC until the finished product oligomer is formed. An exothermic process occurs in the reactor. The oligomer formed in the reactor has a high viscosity and is transferred to the settling device 9 to separate the water contained in it. The settling device is a cylindrical vessel with a conical base and is used in a periodic mode. The raw material is fed from the upper part of the device. After a certain period of 7-10 minutes in the mixing device, the sediment settles to the lower part of the device.

Water is removed from the raw material mixture from the upper part of the settling device through the valve 10. The settled resin is transferred to the belt dryer 11 through a nozzle installed at the bottom of the settling device. The belt dryer consists of 3 Teflon. During the drying process, it is dried by hot air to the required humidity level (20-150 °C).

In the belt dryer, the oligomer is processed until a dry matter content of up to 90% is formed. The dried oligomer is transferred to the hammer crusher 13 via the belt conveyor 12, where the oligomer is ground to a powder of 0.5-1 μm and then transferred to the container 14.

**Discussion and results.** For production purposes, it is advisable to obtain the modified oligomer in the form of a powder or a concentrated solution. Experiments on evaporation and drying of the modified oligomer under various conditions are ineffective. For example, when evaporating the modified oligomer at 100-105 °C, water evaporates very slowly, and the drug loses its solubility. Evaporating the drug at lower temperatures (50-60 °C) leads to the formation of a pasty, opaque, poorly soluble mass in water. Therefore, there is a need to develop a technology for obtaining a concentrated modified oligomer that does not require evaporation, and such oligomers were obtained by us.

Concentrated modified oligomers obtained under production conditions can be used even after 6-7 months. Only in this case, it is advisable to dilute the drug with water before use in order to reduce the viscosity of the solution.

The amount of raw materials required to produce 1 ton of TFO corrosion inhibitor is given in Table 3.

***Table 3***

**Amount of raw materials required to produce 1 ton of TFO corrosion inhibitor**

| TFO corrosion inhibitor components | Consumption of starting materials per 1 ton, kg |
|---|---|



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| | |
|---|---|
| Formalin | 380 |
| Thiosemicarbazide | 383 |
| Orthophosphate | 413 |
| Total | 1 176 |

Table 3 shows that a total of 1176 initial raw materials are used to produce 1 ton of corrosion inhibitor.

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