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ENHANCING DEMULSIFICATION EFFICIENCY AND CORROSION PROTECTION IN OIL INDUSTRY: A STUDY OF NOVEL COMPOSITIONS

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In countries with developed oil industries, the primary objective is to effectively implement the demulsification of water-oil emulsions and provide corrosion protection for facilities during the preparation of heavy oils with stable emulsions for transportation. Consequently, the development of new multi-functional compositions to enhance the efficiency of the emulsion decomposition process and protect the internal surfaces of transport preparation facilities from corrosion remains a pertinent issue. The article presents the results of laboratory experiments on the demulsification of stable water-oil emulsions from the Muradkhanli field in Azerbaijan, which have a dilution rate of 41% (by mass) and provides satisfactory corrosion protection. For the first time, compositions comprising two new ingredients (Alkan-415+Gossypol resin in a 4:1 ratio (denoted as G-1) and Alkan-415+MARZA-1 in a 7:1 ratio (denoted as G-2)) were prepared under laboratory conditions, and their demulsification and corrosion protection effects in an acidic environment were studied. The demulsification process was conducted at temperatures of 50 and 60^{0}C for two hours. During the examination of the demulsification efficiency of the compositions, it was observed that the effectiveness of the reagents increased with higher concentrations. At temperatures of 50 and 60^{0}C, the most significant effects were observed at a concentration of 700 g/t for both compositions. At these temperatures, the residual water content due to the effect of the G-1 composition was 0.02% and 0.01%, and for the G-2 composition, it was 0.01% and 0.005%, respectively. Furthermore, the corrosion protection efficiency of both G-1 and G-2 compositions in an acidic environment was investigated. During the experiment, the highest effectiveness was observed at a concentration of 700 g/t for both compositions. At this concentration, the corrosion protection effect of the G-1 composition was 96%, while that of the G-2 composition was 98%. Thus, it was determined that, due to their multifunctionality and significant impact both in the decomposition of stable water-oil emulsions and in acidic environments, the optimal consumption rates of both compositions with new content are 700 g/t.

Keywords: composition, corrosion, emulsion, oil, demulsifier, deemulsification, dehydration, decomposition, bottle test.

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Introduction

Currently, most of the world's large oil fields and mines have entered their final stage of production, as a result of which oil production becomes difficult, its dilution increases to 80–90%, and the properties of produced oils, especially their viscosity, increase [1,2]. The quality of oils mainly depends on the composition and properties of hydrocarbons, as well as the admixtures in their content. This significantly affects the processing technology, the quality and yield of the obtained oil products, and causes equipment corrosion and poisoning of expensive catalysts. All this ultimately leads to an increase in the cost of oil refining and oil products. Therefore, it is necessary to prepare oil before entering the processing, more precisely, it is necessary to reduce the amount of additives such as water, salts, mechanical admixtures and so on to a minimum. It should be noted that chlorides, chlorine-organic and sulfurous compounds with the presence of water cause rapid corrosion of the internal surface of oil transportation facilities.

Various types of emulsions and their mixtures emerge as a result of mixing of phases during the joint movement of oil, gas and water with oil field communications [3]. Emulsions that are relatively more common in oil and gas industry are mainly considered to be water-in-oil emulsions. The presence of surfactants such as asphaltenes, paraffins, resins and naphthenic acids in the content of oil causes the processes of dispersion of water droplets in oils. Such surfactants are suspended in the dispersed oil system [3–6]. The concentration of existing natural surfactants impacting on the stability of water-oil emulsions is higher in heavy oils than in light oils [7,8].

The processes of oil dehydration and desalination are of great importance in terms of improving oil processing technology and reducing the costs of its transportation. Complications during dehydration and desalination of heavy and highly viscous oils capable of forming stable emulsion systems usually occur due to the presence of various types of admixtures in the content of emulsions, which should be removed by the most efficient methods. The use of multifunctional compositions in the preparation of such oils is expedient, because existing individual reagents used in dehydration and desalination of oil emulsions containing high amounts of various mixtures are less effective.

Modern technology implying the use of demulsifiers is based on complex physical (dissolution, diffusion, sedimentation), physicochemical (adsorption interaction at the boundary of phase separation, coalescence) and colloid-chemical (wetting, peptization, flocculation, etc.) processes. Processing of oil emulsion with demulsifier leads to deep quality changes in its stabilization mechanism and separation of oil emulsion into primary phases. Thus, the purpose of the use of demulsifiers is to ensure effective decomposition of oil emulsions in the distance from group collection points to the commodity tanks of oil collection points [6].

The stability of emulsion is highly dependent on its dispersion. The most stable emulsions have droplet dimensions of 0.1–20 μm. Decomposition of emulsions is associated with serious technological and technical challenges. Emulsions occurring in oil extraction have high viscosity and stability and difficulty of decomposition, which complicate transportation and preparation of oil in the mines [9–12].

Increasing the amount of production of heavy and high-viscosity oils capable of forming stable emulsion systems requires improvement of traditional technologies regarding the preparation of hydrocarbon raw materials for further processing. Complications during dehydration and desalination of such oils, as a rule, occur in the presence of various types of mixtures, which should be removed through the most effective methods. An important aspect in the preparation of this type of oil is to develop multi-functional composition demulsifiers having properties such as corrosion protection of the internal surface of transport preparation facilities and demulsification, and first of all, the study of their efficiency under laboratory conditions. In this regard, preparation and characterization of new multi-functional compositions for decomposition of stable water-oil emulsions and protection of the inner surface of transport preparation facilities from corrosion are considered a very topical issue.

This work was aimed at developing new multi-functional compositions under laboratory conditions and investigating the efficiency of demulsification and corrosion protection.

Experimental

While carrying out laboratory tests, the method of «bottle test» (static deposition) was used [13]. Dehydration of water-oil systems with a reagent was determined by the «bottle test» method in terms of the volume of water released from emulsions at different times. The amount of water in the investigated crude oil was determined by Dina-Stark method.

Laboratory tests were performed taking into account specific technological modes (separation temperature, dehydration time, hydrodynamic properties, dosing, and hydration of products).

The main evaluation criteria are considered dehydration dynamics of oils, the residual amount of water in oils in accordance with SS 39-133-81, the quality (visual) of water and the wall of precipitator-cylinders.

The following compositions were used for the thermochemical deemulsification process in laboratory conditions:

1. Alkan-415+Gossypol resin in a 4:1 ratio (denoted as G-1);
2. Alkan-415+MARZA-1 in a 7:1 ratio (denoted as G-2).

Being a product of Azerbaijan, Alkan-415 is used as a demulsifier in oil industry and is a blocking copolymer of simple and complex ethers. Alkan-415 reagent is a transparent yellow-brown liquid, the freezing temperature of which being -38^{0}C. It smells as specific solvents. Gossypol resin reagent is a residue left after the production of cottonseed oil and is used in oil industry to protect the internal surface of facilities from corrosion. MARZA-1 is a reagent of organic origin with triple bonds the molecules of which are composed of carbon, hydrogen, halogen and oxygen element atoms. The reagent was synthesized by Azerbaijani researchers and is used as a multifunctional reagent in corrosion protection [14].

Tested emulsion samples are placed in a specially graduated 100 ml precipitator with a conical bottom, to each of which is added a pre-calculated amount of demulsifiers in commodity form (supply form) by means of syringe-micro-dosers. The precipitators are closed tightly and shaken by hand for 10 minutes to evenly distribute the demulsifiers in the volume of oil phase.

The calculation of demulsifier doses is carried out according to the initial dilution of water-oil emulsions without considering the concentration of the demulsifier and the concentration of oils.

Optimal consumption rate during laboratory testing of compositions were as follows: 200, 250, 200, 350, 400, 450, 500, 550, 600, 650, and 700 g/t. Experiments were carried out at temperatures of 50 and 60°C for 45, 90, 150, 200, and 240 minutes.

The volume of demulsifier solution dosed in the emulsion weight is calculated according to the following formula:

$$V_d = \frac{m(100 - W_{or})O_p}{1000}, \qquad (\mu l)$$

where m is the weight of emulsion (ml); O_p is the given dose of demulsifier (g/t); and W_{or} is the initial average degree of emulsion hydration (%).

After being mixed in the shaker, the precipitators with water-oil emulsions treated with demulsifiers are placed in the thermostat for the period of time corresponding to their stay in the pipelines and technological oil production facilities. Thermostating temperature corresponds to the technological dehydration temperature mode of oils. The amount of separated water is recorded at pre-selected time intervals. In addition, the quality of water separated after dehydration of oils is visually analyzed. Then, using a special sampler, an oil sample is taken to determine the amount of residual water at a level 10 mm above «oil–water» phase separation boundary (SS 2477-65). Based on the volume of water separated over time, knowing the initial hydration degree of water-oil emulsions, dehydration degree of emulsions is calculated as follows:

$$\text{hydration degree (\%)} = \frac{\text{volume of separated water}}{\text{initial dilution rate}} \cdot 100\% .$$

The methodology of determining the efficiency of demulsifiers under laboratory conditions was arranged by comparative tests. The purpose of current tests is to select a relatively more effective product from a number of tested products.

Experiments were conducted on dehydration of oil emulsions of Muradkhanli field with a dilution rate of 41% (by mass) under laboratory conditions.

Brief characteristics of Muradkhanli field oils are shown in Table 1.

Table 1

Physicochemical properties of Muradkhanli oils

Parameter	Quantity
Density, ρ_4^{10}, kg/m^3	947.3
Amount of paraffin, wt.%	5.8
Amount of resin, wt.%	18.1
Amount of asphaltenes, wt.%	4.5
Mechanical mixtures, wt.%	5.86
Viscosity 20^{0}C, mPa·s	2157.3
Sulfur content, wt.%	0.28
The amount of chlorine salts, mg/l	534.3
Freezing temperature, ^{0}C	+9
Amount of water, wt.%	41

The selection of this oil is related to the fact that chemical reagents are used to increase oil bearing in the existing field, and their use leads to an increase in the stability of water-oil emulsions. In addition, existing oil has both paraffinic and resin-asphalt type stabilizers and forms stable emulsion systems over time.

In addition, corrosion protection properties of compositions G-1 and G-2 in the formation water containing hydrogen sulfide (acidic environment) were investigated. The corrosion rate was calculated according to the following mathematical expression:

$$K = \frac{m_1 - m_2}{S \cdot \tau},$$

where m_1 is pre-test weight of a sample (g); m_2 is the weight of the sample after removing the corrosion product (g); S is the area of the sample (m^2); and τ is the duration of test (h).

Expression used to calculate the inhibition factor is as follows:

$$\gamma = \frac{K_0}{K_{inh}},$$

where K_0 is the corrosion rate in a non-composite environment and K_{inh} is the corrosion rate in the composition-based environment (g/m^2·h).

The protection effect of the composition was calculated by the following formula:

$$Z = \frac{K_0 - K_{inh}}{K_0} \cdot 100\%,$$

where K_0 is the corrosion rate in a non-composite environment, and K_{inh} is the corrosion rate in the composition-based environment (g/m^2·h).

Based on the corrosion rate, the penetration depth is determined as follows:

$$K_p = \frac{8760 K_m}{\rho} \cdot 10^{-3},$$

where K_p is the penetration rate (mm/year); K is the corrosion rate (g/m^2·h); ρ is the density of investigated metal (g/cm^3); and 8760 is the conversion factor (hours per year).

Results and discussion

In order to separate water from stable water-oil emulsions under laboratory conditions, a relatively simple method, a chemical method at atmospheric pressure with the application of demulsifiers, was used. A relatively rapid method of comparative evaluation of the demulsification activity of chemical reagents is considered to be the widespread method of "bottle test". As a result of laboratory tests, the dynamics of water separation and the degree of residual hydration of oil phase (depth of oil dehydration) were evaluated.

Demulsification efficiency of two new multifunctional compositions prepared under laboratory conditions at temperatures of 50 and 60^{0}C was studied. The total duration of deemulsification process was determined, it was 120 minutes.

Tables 2 and 3 show the dynamics of water separation due to the impact of G-1 and G-2 compositions at temperature of 50^{0}C and the residual amount of water at different concentrations of the compositions.

As can be seen from Tables 2 and 3, the amount of residual water in oil decreases to a minimum as the concentration of the compositions in stable water-oil emulsions and the duration of deemulsification process increase. Thus, the amount of residual water in the concentration range of 200 to 700 g/t of the compositions changes in the range of 7.0–0.07% and 5.5–0.05% as a result of the effect of composition G-1 and G-2, respectively.

Decomposition process of oil emulsions taken from Muradkhanli field in the presence of compositions was studied under laboratory conditions at temperature of 60^{0}C and the obtained results are presented in Table 4. The following amounts of the compositions were used for the process: 400, 450, 500, 550, 600, 650 and 700 g/t.

The data given in Table 4 show that the compositions significantly reduce the amount of residual water in oil, having higher efficiency at temperature of 60^{0}C. During the deemulsification process at the specified temperature, the amount of residual water in stable oil emulsions in the concentration range of 400–700 g/t of compositions varies in the range of 0.9–0.05% and 0.6–0.03% with the participation of compositions G-1 and G-2, respectively.

Electrochemical corrosion protection properties of new compositions G-1 and G-2 in acidic

Table 2

Demulsification effect of composition G-1 at temperature of 50^{0}C

Reagent	Reagent consumption, g/t	The amount of water released depending on time (minutes), %				Amount of residual water, %	
		30	60	90	120	Before deemulsification	After deemulsification
without reagent	–	26.0	33.0	40.0	44.0	41	56
G-1	200	41.1	54.2	75.1	93.0	41	7.0
	250	42.2	64.0	89.3	96.5		3.5
	300	45.0	70.4	91.0	96.8		3.2
	350	57.3	76.2	92.3	98.1		1.9
	400	59.2	85.4	94.1	98.5		1.5
	450	61.6	91.4	96.0	98.9		1.1
	500	68.7	93.8	97.9	99.1		0.9
	550	75.3	96.5	98.1	99.6		0.4
	600	78.6	97.8	98.9	99.8		0.2
	650	83.7	98.82	99.84	99.85		0.15
	700	86.3	99.90	99.91	99.93		0.07

environment were also studied. The samples of St 3 brand steel (Table 5) were used to study the corrosion intensity in acidic formation water environment.

Researches were conducted under laboratory conditions at temperature of 25^{0}C at consumption rates of 300, 400, 500, 600 and 700 g/t of compositions G-1 and G-2 for 6 hours in order to determine the corrosion rate of St3 brand steel plates with dimensions of 30×20×1 mm in terms of mass loss.

St3 brand steel plates were polished on a grinding machine and after their surfaces having been cleaned with acetone and alcohol, they were weighed on an

Table 3

Demulsification effect of composition G-2 at temperature of 50^{0}C

Reagent	Reagent consumption, g/t	The amount of water released depending on time (minutes) %				Amount of residual water, %	
		30	60	90	120	Before deemulsification	After deemulsification
without reagent	–	26.0	33.0	40.0	44.0	41	56
G-2	200	43.2	56.4	77.5	94.5	41	5.5
	250	44.4	66.2	87.5	97.7		2.3
	300	47.2	72.6	92.2	98.2		1.8
	350	59.5	78.4	94.6	98.8		1.2
	400	61.3	85.6	96.3	99.1		0.9
	450	63.8	91.6	97.2	99.4		0.6
	500	67.9	93.1	98.1	99.7		0.3
	550	77.6	95.3	99.5	99.9		0.1
	600	80.8	97.76	99.84	99.92		0.08
	650	85.9	98.82	99.87	99.94		0.06
	700	88.7	99.86	99.91	99.95		0.05

Table 4

Demulsification effect of compositions G-1 and G-2 at temperature of 60^{0}C

Reagent	Reagent consumption, g/t	he amount of water released depending on time (minutes), %				Amount of residual water, %	
		30	60	90	120	Before deemulsification	After deemulsification
G-1	400	63.6	89.8	94.2	99.1	41	0.9
	450	69.1	92.6	96.8	99.3		0.7
	500	73.6	95.0	97.2	99.6		0.4
	550	79.8	97.1	98.4	99.8		0.2
	600	83.8	98.72	99.80	99.91		0.09
	650	87.9	99.72	99.87	99.93		0.07
	700	90.5	99.87	99.92	99.95		0.05
G-2	400	65.7	94.8	97.1	99.4	41	0.6
	450	69.9	96.8	98.2	99.6		0.4
	500	77.6	97.2	99.5	99.9		0.1
	550	84.7	98.68	99.77	99.91		0.09
	600	87.9	99.76	99.88	99.94		0.06
	650	94.8	99.87	99.92	99.96		0.04
	700	97.6	99.91	99.94	99.97		0.03

Table 5

Chemical composition of St 3 brand steel

Component	C	Mn	Si	P	S	Cr	Ni	Cu	Fe
Ciontent, wt.%	0.2	0.5	0.15	0.04	0.05	0.30	0.20	0.20	98.36

analytical balance. The experiments were carried out in parallel under the same conditions for comparison, both without the composition and with the addition of the composition. The results obtained during the experiment are given in Table 6.

As is seen from Table 6, both compositions exhibit high protection effect in aggressive acidic corrosion environment. The highest protection effect is observed at the amount of 700 g/t of both compositions. The protection effect at the specified concentration is 96% and 98% for composition G-1 and G-2, respectively.

Thus, for the first time, the properties of new compositions G-1 and G-2 prepared from chemical reagents of various purposes, their multi-functionality were investigated. High efficiency of these compositions both in the decomposition of stable water-oil emulsions and in protecting against electrochemical corrosion in acidic environment were established. The optimal consumption rates of 700 g/t was determined. The results obtained under laboratory conditions provide a basis for proposing the use of compositions G-1 and G-2 in the decomposition of stable water-oil emulsions of heavy oils in mining, and in the protection of the internal surfaces of transport preparation facilities from corrosion.

Conclusions

1. For the first time, multifunctional compositions G-1 and G-2 were prepared using Alkan-415, Gossypol resin, and MARZA-1 chemical reagents, and their impact on the deemulsification of stable water-oil emulsions of Muradkhanli field and the rate of electrochemical corrosion in acidic environment was studied under laboratory conditions.

2. Demulsification process of compositions G-1 and G-2 was carried out at temperatures of 50 and 60^{0}C for two hours. Their demulsification efficiency increases as the concentration of reagents varies in the range of 200–700 g/t.

3. It was determined that the highest demulsification effect is observed at concentration of 700 g/t of both compositions. The amount of residual water at temperatures of 50 and 60^{0}C in the specified concentration of composition G-1 was 0.07% and 0.05%, and it was 0.05% and 0.03% for composition G-2, respectively.

4. It was determined that both compositions have a high degree of protection properties. The highest protection effect was recorded at concentration of 700 g/t of the compositions. The protection effect of composition at optimal consumption rate was 96% and 98% for G-1 and G-2, respectively.

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Table 6

Protection effects of compositions G-1 and G-2 in the formation water in acidic environment

Consumption rate, g/t	K, g/m^2·h		Inhibition factor, γ	K_p, mm/year	Protection effect, Z, %
	without reagent	with reagent			
G-1 composition					
0.0	1.4680	–	–	–	–
300	1.4680	0.7046	2.08	0.7891	52
400	1.4680	0.5138	2.85	0.5754	65
500	1.4680	0.3229	4.54	0.3616	78
600	1.4680	0.2055	7.14	0.2301	86
700	1.4680	0.0587	25.00	0.0657	96
G-2 composition					
0.00	1.4680	–	–	–	–
300	1.4680	0.5872	2.50	0.6576	60
400	1.4680	0.4110	3.57	0.4603	72
500	1.4680	0.2348	6.25	0.2629	84
600	1.4680	0.1174	12.50	0.1314	92
700	1.4680	0.0293	50.10	0.0328	98

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ПІДВИЩЕННЯ ЕФЕКТИВНОСТІ ДЕЕМУЛЬГУВАННЯ ТА ЗАХИСТУ ВІД КОРОЗІЇ В НАФТОВІЙ ПРОМИСЛОВОСТІ: ДОСЛІДЖЕННЯ НОВИХ КОМПОЗИЦІЙ

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У країнах з розвиненою нафтовою промисловістю першочерговим завданням є ефективна реалізація деемульгації водонафтових емульсій і забезпечення антикорозійного захисту об'єктів під час підготовки важких нафт зі стабільними емульсіями до транспортування. Отже, розробка нових багатофункціональних композицій для підвищення ефективності процесу розкладання емульсій та захисту внутрішніх поверхонь засобів транспортної підготовки від корозії залишається актуальною. У статті наведені результати лабораторних експериментів з деемульгації стійких водонафтових емульсій родовища Мурадханли в Азербайджані, які мають ступінь розбавлення 41% (за масою) і забезпечують задовільний захист від корозії. Вперше охарактеризовані композиції з двох нових інгредієнтів (Алкан-415+смола Gossypol у співвідношенні 4:1 (позначається Г-1) та Алкан-415+МАРЗА-1 у співвідношенні 7:1 (позначається Г-2)) були виготовлені в лабораторних умовах і досліджено їх деемульгаційну та антикорозійну дію в кислому середовищі. Процес деемульгування перебігав при температурах 50 і 60^{0}C протягом двох годин. Під час перевірки ефективності деемульгування композицій було помічено, що ефективність реагентів зростає з більш високими концентраціями. При температурах 50 і 60^{0}C найбільш значні ефекти спостерігалися при концентрації 700 г/т для обох композицій. При цих температурах залишковий вміст води за рахунок дії композиції Г-1 становив 0,02% і 0,01%, а для композиції Г-2 відповідно 0,01% і 0,005%. Крім того, досліджено антикорозійну ефективність композицій Г-1 і Г-2 у кислому середовищі. Під час експерименту найвищу ефективність спостерігали при концентрації 700 г/т для обох композицій. При цій концентрації антикорозійний ефект композиції Г-1 становив 96%, а композиції Г-2 – 98%. Таким чином, встановлено, що завдяки їх багатофункціональності та значному впливу як при розкладанні стійких водонафтових емульсій, так і в кислому середовищі, оптимальні норми витрати обох композицій з новим вмістом становлять 700 г/т.

Ключові слова: склад, корозія, емульсія, масло, деемульгатор, деемульгація, зневоднення, розкладання, пляшковий тест.

ENHANCING DEMULSIFICATION EFFICIENCY AND CORROSION PROTECTION IN OIL INDUSTRY: A STUDY OF NOVEL COMPOSITIONS

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In countries with developed oil industries, the primary objective is to effectively implement the demulsification of water-oil emulsions and provide corrosion protection for facilities during the preparation of heavy oils with stable emulsions for transportation. Consequently, the development of new multi-functional compositions to enhance the efficiency of the emulsion decomposition process and protect the internal surfaces of transport preparation facilities from corrosion remains a pertinent issue. The article presents the results of laboratory experiments on the demulsification of stable water-oil emulsions from the Muradkhanli field in Azerbaijan, which have a dilution rate of 41% (by mass) and provides satisfactory corrosion protection. For the first time, compositions comprising two new ingredients (Alkan-415+Gossypol resin in a 4:1 ratio (denoted as G-1) and Alkan-415+MARZA-1 in a 7:1 ratio (denoted as G-2)) were prepared under laboratory conditions, and their demulsification and corrosion protection effects in an acidic environment were studied. The demulsification process was conducted at temperatures of 50 and 60^{0}C for two hours. During the examination of the demulsification efficiency of the compositions, it was observed that the effectiveness of the reagents increased with higher concentrations. At temperatures of 50 and 60^{0}C, the most significant effects were observed at a concentration of 700 g/t for both compositions. At these temperatures, the residual water content due to the effect of the G-1 composition was 0.02% and 0.01%, and for the G-2 composition, it was 0.01% and 0.005%, respectively. Furthermore, the corrosion protection efficiency of both G-1 and G-2 compositions in an acidic environment was investigated. During the experiment, the highest effectiveness was observed at a concentration of 700 g/t for both compositions. At this concentration, the corrosion protection effect of the G-1 composition was 96%, while that of the G-2 composition was 98%. Thus, it was determined that, due to their multifunctionality and significant impact both in the decomposition of stable water-oil emulsions and in acidic environments, the optimal consumption rates of both compositions with new content are 700 g/t.

Keywords: composition; corrosion; emulsion; oil; demulsifier; deemulsification; dehydration; decomposition; bottle test.

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