Creation of aerosolized detergent compositions for protecting high-precision metal mirrors from the impact of adverse climate factors

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Abstract. This article is devoted to creation of aerosolized detergent compositions, needful for use during operation of high-precision metal mirrors, as a rule, in field conditions. The created detergent compositions with inhibitory properties allow, simultaneously with carrying out the process of physicochemical cleaning of optical surface from technological impurities, to ensure its protection from the influence of adverse climatic factors during storage, transportation, installation and exploitation of the element with the possibility of its alignment. The high climatic resilience of the protective films investigated in this article, which are formed during the cleaning of the optical surface, is shown. In this case, the optical characteristics of the processed elements after climatic tests do not get worse.

1. Introduction

The process of physicochemical cleaning of high-precision details made from non-ferrous metals must provide surface protection from the ingress of impurities on it, which degrade the surface characteristics during storage, installation, transportation and operation, as well as from the influence of adverse climatic factors. The requirements for protective coatings on the optical surface have a number of significant features.

Since in this work the study of the physicochemical cleaning of high-precision details made of non-ferrous metals, using the example of metal mirrors of high-power gas lasers [1-4], was carried out, further we will consider, first of all, the optical characteristics of the mirrors.

First of all, coating formed during cleaning, must: reliably protect the optical surface, during the entire service life of the element, from the influence of adverse climatic factors; be non-toxic and chemically inert (should not interact with the element material and not degrade optical parameters); easy to apply on the optical surface and remove from it, if necessary; be workable in a wide range of operating temperatures of the optical element. Specific requirements related to the protection of the optical surface of high-precision non-ferrous metal details is that the protective coating should not degrade the energy characteristics of the details during exploitation.

An ideal protective coating for high-precision non-ferrous metal details would be a coating that meets all of the listed requirements, applying of which would be carried out simultaneously with the process of physicochemical cleaning of the optical surface.
The literature describes a number of methods for protecting metal products during operation. A method for protecting the surface of metal products from atmospheric corrosion in a sealed volume, using vapor-phase inhibitors on porous carriers [5], was proposed. The described method is quite effective for the protection of optical elements, but requires a sealed special container for both elements and inhibitors.

Methods for protecting the optical surface of metals, using coatings that are inert to atmospheric corrosion, for example, oxides, are widely known [6, 7]. However, these methods require specialized coating equipment and expensive coating materials; moreover, these coatings are difficult to remove if necessary.

Method of electrochemical protection the surface of metal products is known from the literature [8]. However, this method is not sufficiently reliable in protecting the optical surface of chemically active metals (copper and its alloys) and requires additional devices to bring a more active element into contact with the metal to be protected.

There is a well-known method of chemical surface modification by replacing active surface groups (for example, OH− on the inactive ones, such as OCH3 or OS (CH3)3, etc.), or by grafting large inert groups according to the reaction [9]:

\[
\begin{align*}
\text{Si}^+ \text{CH}_3 + \text{ClSi} \text{(CH}_3)_3 \rightarrow \text{Si}^+ \text{Si}^{++} \text{Si}^- \text{HCl} \\
-\text{Si}^- + \text{ClSi} \text{(CH}_3)_3 = -\text{Si}^- + \text{HCl}
\end{align*}
\]  

(1)

Such modification dramatically reduces the adsorption energy not only of molecules capable of specifically interact with hydroxyl groups, for example, nitrogen, ethylene, benzene, ether, alcohols, etc., but also of all molecules in general. When such modifying layers are formed, the adsorbate molecules cannot react directly with the atoms of the solid surface on which the modifying layer is applied, since steric difficulties arise. The reason for this is that the distance between adjacent CH3 groups in the modifying layer corresponds to Van der Waals dimensions, and the distance between oxygen and silicon atoms in the silica lattice is much shorter. However, surface modification requires the selection of an appropriate substance for this purpose for a specific surface and the solution of the problem of its subsequent removal.

To protect optical elements at various stages of manufacture, removable protective varnishes of the "chemically resistant" brand are currently widely used, the applied films of which, if necessary, are capable of being removed by a "stockade", as well as organofluorine polymers, for example, fluoroplastic, as well as nitrocellulose-based enamel and other similar compositions [10-12]. The disadvantage of these protective coatings is their long drying time after application. After removal (cohesive detachment), several monolayers of the protective coating remain on the optical surface, which can cause a decrease in the optical resilience threshold of elements, when impacted to high-energy radiation as a result of burnout of the substance of coating residues.

Inhibitors, based on various organic compounds or their mixtures, are quite effective way for protecting metal surfaces. Among said organic compounds, azoles, triazoles and their derivatives are currently most widely used as inhibitors. The use of these types of organic compounds as a protective coating allows you to provide effective protection of the surface of metals from copper, aluminum, and their alloys, as well as other similar materials. At the same time, the protective film is low toxic, inert, easily removable and does not leave marks on the optical surface after removal. However, at present, there are no compositions that are capable, simultaneously with the process of physicochemical cleaning of optical elements, provide their protection from contamination during transportation, storage, installation and operation, as well as protection from corrosion under the influence of unfavorable climatic factors.

In [13, 14], it is noted, that 1,2,3-benzotriazole and its derivatives occupy a special place in terms of the protective effect in relation to copper and its alloys, some other non-ferrous metals and steel. The anticorrosive effect of 1,2,3-benzotriazole is caused by the formation of a protective polymer film on
the metal surface, which effectively protects the surface from both corrosion in solutions and atmospheric corrosion. The film is a water-insoluble copper complex with a stoichiometric ratio of copper to 1,2,3-benzotriazole (BTA) equal to 1:1, which has the empirical formula C₆H₄N₃Cu[Cu(I)BTA]. At the same time, the copper atom is captured through coordination bonds with nitrogen atoms into the triazole ring, forming a two-toothed structure, and the mobile hydrogen atom in the NH group is replaced by copper.

It should be noted, that BTA has the greatest anticorrosive effect in the neutral solution, since the reaction [15]:

\[ \text{Cu}^+ + \text{BTA} \rightarrow \text{BTA} - \text{Cu(I)} + H^+ \]

in the neutral solution flows to the right, and in an acidic solution - to the left, i.e., the inhibitory effect is due to the formation of the copper salt of benzotriazole BTA-Cu(I).

In view of the above, a number of experimental studies have been carried out. Their goal is to elucidate the effect of detergent compositions with inhibiting additives, both on the degree of chemical cleaning with their help of the optical surface from technological contaminants, and on the inhibiting and energy properties of the optical surface treated in this way.

2. Experimental technique

Optical elements made of oxygen-free copper and AL-9 aluminum alloy were selected as test objects. The following compositions were used as detergent compositions: № 1 "freon-114B2 (50 % vol.) - methylene chloride (20 % vol.) - ethanol (22 % vol.) - acetone (8 % vol.) - BTA (0.01 g)"; № 2 "0.01 % wt. solution of N-methylphthalimide in acetone"; № 3 "0.01 % wt. solution of N-methylmaleimide in acetone"; № 4 "0.001 % wt. solution of N-octadecynaphthylimide in acetone". All compositions were placed in 180 ml aerosol containers. Freon-12 was used as a propellant. The aerosol composition is as follows: "washing composition - 70% by wt., freon-12 – 30 % wt."

In As shown by preliminary tests, the use of imides with large hydrocarbon radicals for anticorrosion protection is impractical. When using them, the optical surface reduces its energy characteristics (the plasma formation threshold decreases). These imides are opaque in the visible region of the spectrum. Therefore, in the experiments described below, in addition to BTA, various imide compounds with methyl hydrocarbon radicals were used as inhibiting additives.

According to the theory of regular solutions [16], if there are molecules of two kinds, characterized only by dispersion interaction, after mixing them under conditions of a zero value of the excess volume (\( \Delta V^M = 0 \)) and disorder distribution of orientation of molecules (excess entropy of mixing \( \Delta S^M = 0 \)), the cohesion energy of one mole of the resulting liquid mixture can be expressed as:

\[
-E^M = \frac{c_{11}V_1^2x_1^2 + 2c_{12}V_1V_2x_1x_2 + c_{22}V_2^2x_2^2}{V_1x_1 + V_2x_2}
\]

(3)

In this equation, the internal energy (\( E_i \)) of a two-component solution acts as a quadratic function of volume fractions (\( x_i \)), volume (\( V_i \)) is expressed using the average mole fractions of pure components (\( \Delta V^E = 0 \)), \( (c_{ij}) \) describes the interaction of pairs of molecules "i-j", \( c_{11} \) and \( c_{12} \) are functions of temperature only. For a pure single component solvent, this expression has the form:

\[
-E_i = c_{11}V_1, \quad \text{whence} \quad c_{11} = \frac{-E_i}{V_1}
\]

(4)

As far as, at the temperature of the liquid phase, the cohesion energy can be considered approximately equal to the evaporation energy (\( \Delta E_i^V \)), then (4) can be rewritten as:
\[ c = \frac{\Delta E^V}{V}, \]  

where \( V \) - is the molecular volume of the solvent.

Since \( (c) \) is the cohesion energy per unit volume, it can be called the "specific bulk density of cohesion energy". There is a strong interaction between both components in solution. Moreover, if the molecular volumes \( (V) \) of both components differ significantly, and the energy of thermal motion is significantly greater than the cohesion energy, it could be considered, that the entropy of mixing \( (\Delta S_{FH}^M) \) is maximal, and is determined by the Flory-Higgins expression:

\[ \Delta S_{FH}^M = -R \left( x_1 \ln \varphi_1 + x_2 \ln \varphi_2 \right), \]  

and the activity of component "1" can be represented as:

\[ \ln a_1 = \ln \varphi_1 + \varphi_2 \left( 1 - \frac{V_1}{V_2} \right) + \frac{V_1 \varphi_2 (\delta_1 - \delta_2)^2}{RT}, \]

\[ \ln a_2 = \ln \varphi_2 + \varphi_1 \left( 1 - \frac{V_1}{V_2} \right) + \frac{V_2 \varphi_1 (\delta_1 - \delta_2)^2}{RT}. \]

Several methods are used to calculate the solubility parameter \( (\delta) \). For example, the value of the evaporation energy and molar volume allows calculating the main parameters of the theory of regular solutions - density of cohesion energy and \( (\delta) \). Taking into account the relationship between the energy and the latent heat of evaporation \( (\Delta H_g^V) \) at temperature \( T \), the expression for \( (\delta) \) is:

\[ \delta = \left( \frac{\Delta H_g^V}{RT} \right)^{\frac{1}{2}}, \]

An example of the efficiency of application \( (\delta) \) is the interaction between solvents and polymers. Since on the surface of metal optics contaminants with different properties are present, as a rule, together, in order to increase the affinity of the dissolving medium for contamination and in accordance with economic and technological requirements, it is necessary to use solvent mixtures during cleaning. To calculate \( (\delta) \) a mixture of solvents, the expression [17] was used:

\[ \delta_{mix} = \frac{x_1^MV_1^M \delta_1 + x_2^MV_2^M \delta_2 + \ldots + x_i^MV_i^M \delta_i}{x_1^MV_1^M + x_2^MV_2^M + \ldots + x_i^MV_i^M}, \]

where \( V^M \) - is the molar fraction of the component, calculated as:

\[ x_i = \frac{c_i}{M_i}, \]

\[ \frac{c_1}{M_1} + \frac{c_2}{M_2} + \ldots + \frac{c_i}{M_i}, \]

here \( c_i \) - is the concentration of the component, % wt; \( M_i \) - molecular weight.

From (10) it can be seen, that with equal molar volumes \( (\delta_{mix}) \) - is the additive value. Even at different molar volumes \( (V^M) \), it can be approximately considered, that on the plane with the coordinates of the solubility parameters, the point corresponding to the solubility parameter of the mixture \( (\delta_{mix}) \) lies on the straight line that connects the points with the coordinates of the components. This makes it possible approximately carry out the choice of the detergent medium by a graphical method. These techniques make it possible to widely use \( (\delta) \) of different solvents for the selection of detergents to clean metal optics from contamination and to increase the affinity of the dissolving medium for contamination. The
greatest advantage have azeotropic mixtures, characterized by both unchanged composition and boiling point. This makes it cheaper and easier to clean metal optics and regenerate solvents.

3. Experimental results and discussion

Papers [1-4, 18-20] report about our studies devoted to the possibility of extending the service life of high-precision copper (Mob) mirrors of high-power CO₂ lasers by periodic (or as required) physicochemical treatment with specially created azeotropic mixtures. Based on our studies, we have created a number of compositions to clean the optical surface with inhibiting properties in aerosol containers in the form of azeotropes of the following composition: № 1 – "freon-114B2 - methylene chloride - ethanol - aceton – BTA"; № 2 – "freon-114B2 - aceton - tert-butyl alcohol - N,N-dimethylimidazole benzene 1,2,4,5-tetra carboxylic acid"; № 3 – "0.01 % wt. solution of N-methylmaleimide in aceton"; № 4 - "0.001 % wt. solution of N-octadecynaphthylimide in aceton".

All of these compositions were developed on the basis of the proximity of their solubility parameter (δ) to the solubility parameter of the corresponding contamination (δ₁) adjusted for for the polar selectivity of the composition components and contamination and the energy characteristics of the processed surface. In particular, the detergent composition in the form of an azeotropic mixture, which has the following composition: "freon-114B2 (50% vol.) - methylene chloride (20 % vol.) - ethanol (22 % vol.) - aceton (8 % vol.)" (solubility parameter δ = 19.0 J1/2 cm3/2), used mainly to remove treeceanylol resins, together with a given amount of BTA were placed in an aerosol container. All of said solvents or were branded "particularly clean", or previously passed rectification purification. Optical elements were treated with ethyl alcohol, using standard technology. Then twice, at a consumption of the detergent composition ~ 4 ml/cm², they were cleaned with compositions № 1, 2, 3, 4 by aerosol spraying, until the optical surface was completely covered.

Tests for mechanical, adhesive strength and resistance to climatic factors of the protective films of BTA, N-methylmaleimide, N-methylphthalimidimide and N-octadecynaphthylimide, formed as a result to clean with detergent compositions, containing inhibiting additives, were carried out according to the following procedure.

After drying of the formed protective coating, adhesion strength tests were carried out by detachment of the adhesive tape (state standard 20477-75) to the protective film. Mechanical strength was measured on the device SM-55 according to industry standard 3-190I-81 and for resistance to climatic factors - according to state standard 9.401-79. In addition, the protective coating was tested for exposure to continuous irradiation by xenon lamps with an integral heat flux density of 1125 W·m⁻², including by UV flux density of 42 W·m⁻² for 10 hours.

Further, the mirrors were cleaned with ethyl alcohol, followed by cleaning the mirrors with detergent compositions and protective coatings application on them. After carrying out climatic tests and removing the protective coatings with ethyl alcohol by watering, on the optical elements, the specular reflection coefficient was measured at a wavelength of 10.6 μm. Then, ellipsometric measurements were carried out at a wavelength of 0.63 μm, on the basis of which the optical characteristics (n, k, R₆₃) of the surface were calculated. Next on the samples we controlled: the chemical purity of the optical surface - on an EF-ZMA electronic fluorometer (indirect method), the geometric shape (N, ΔN) and optical purity (P).

The values of optical constants and chemical purity of optical surface of elements before and after climatic tests are presented in Table 1.

The results presented in Table 1 show that the specular reflection coefficients at wavelengths of 10.6 μm and 0.63 μm for all samples (except the control ones) did not change, within the measurement error, after climatic tests and removal of the protective coating. The specular reflection coefficient at a wavelength of 10.6 μm of the control samples (examples No. 1, 5), which were not treated with the composition No. 1 with the inhibiting additive BTA and passed climatic tests, remained unchanged within the measurement error. However, the reflectance at 0.63 μm decreased by 12% for copper and 4.4% for AL-9 aluminum alloy. Control of the chemical purity of the optical surface after removing the protective coating showed that the amount of technological contaminants present on it decreased for
metals and alloys by 4 orders of magnitude, for crystals - by 3 orders of magnitude compared to the amount of contaminants present on the surface before treatment with the composition No. 1. The amount of contaminations on the optical surface of the control elements after climatic tests increased 5 times. Studies of optical parameters (N, ΔN, P) after conducting climatic tests and removal of the protective coating showed, that their parameters remained unchanged.

**Table 1.** The values of optical constants and chemical purity of optical surface of elements before and after climatic tests after treatment with composition № 1

| Sample № (material) | Data of ellipsometric measurements | Specular reflection coefficient | Fluorometric method |
|---------------------|-----------------------------------|-------------------------------|-------------------|
|                     | after cleaning with ethanol        | after treatment with          | after climaic tests and removing the protective coating |
|                     |                                   | composition № 1,             | after cleaning with ethanol after climatic tests with ethanol |
|                     |                                   | conducting climatic tests    | after cleaning with ethanol after climatic tests and removing the protective coating |
| №1* (control.)      | 0.13 2.51 93.0                    | 0.45 1.58 81.0               | 99.1 99.0 1·10^-4 5·10^-4 |
| №2*                 | 0.21 3.05 92.1                    | 0.19 3.15 93.1               | 99.1 99.1 1·10^-4 1·10^-7 |
| №3*                 | 0.25 3.05 90.4                    | 0.24 2.75 89.4               | 99.1 99.1 1·10^-4 1·10^-7 |
| №4*                 | 0.21 3.15 91.8                    | 0.21 3.05 92.5               | 99.1 99.1 1·10^-4 1·10^-7 |
| №5 (AL-9) (control.)| 0.83 3.08 74.4                    | 0.74 2.86 70.0               | 97.6 97.5 1·10^-4 5·10^-4 |
| №6 (AL-9)           | 0.99 5.71 89.4                    | 1.10 5.75 88.4               | 97.6 97.9 1·10^-4 1·10^-7 |
| №7 (AL-6)           | 0.97 4.30 82.9                    | 0.97 4.40 83.0               | 97.5 97.5 1·10^-4 1·10^-7 |
| №8 (AL-24)          | 1.41 4.81 82.1                    | 1.35 4.80 81.1               | 97.6 97.6 1·10^-4 1·10^-7 |
| №9 (NaCl)           | 1.51 0.02 4.10                    | 1.52 0.07 4.20               | - - 1·10^-4 1·10^-7 |
| №10 (NaCl)          | 1.48 0.02 3.90                    | 1.50 0.05 4.00               | - - 1·10^-4 1·10^-7 |

* Oxygen-free copper. Control samples No. 1 and 5 passed climatic tests without treatment with composition № 1. The reflection coefficient at a wavelength of 0.63 μm was calculated from the data of ellipsometric measurements by the formula:

\[ R_{0.63} = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]  

**4. Conclusion**

We found a high climatic resistance of the protective films formed in the process to clean the optical surface. In this case, the optical characteristics of the processed elements after the climatic tests do not deteriorate. Control optical elements, not treated with detergent compositions with inhibiting additives, after climatic tests significantly (by 4-12%) worsened their optical parameters.

Detergent compositions with inhibiting properties, allowing, simultaneously with the process of physicochemical cleaning of the optical surface from technological impurities, to ensure its protection from the effects of unfavorable climatic factors during storage, transportation, installation and operation of the element with the possibility of adjusting it without removing the protective coating formed during to clean, have been created.

This technology can be applied not only when working with laser mirrors, but also with other high-precision products made of non-ferrous metals.

**Acknowledgments**

This work was carried out using the resources of the Center for Collective Use of Tver State University in the framework of the state assignment for scientific activity (No 0057-2019-0005 and No 0817-2020-0007).
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