Creation of aerosolized detergent compositions for cleaning high-precision metal mirrors

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Abstract. We report on a studies on the possibility of extending the service life of products of non-ferrous metals by physical and chemical treatments with specially created azeotropic compositions. These studies were carried out on high-precision copper mirrors for high-power CO₂ lasers, exposed during operation to different climatic influences, worsening of their operational characteristics. The results obtained in this paper can be applicable for physical and chemical cleaning of such mirrors and other high-precision parts from non-ferrous metals. The work is devoted to the creation of aerosol detergent compositions intended for use during the operation of mirrors in the field climatic conditions. It is shown that when aluminium and tin-plate aerosol containers are used, compositions that are used to clean metal mirrors should not contain chlorine-substituted hydrocarbons or even “traces” of water and hydroxyl ions. In addition to copper mirrors, optical elements made of other materials were also studied in this work.

1. Introduction

Variety of precision parts from non-ferrous metals are widely used in modern science and technology. The cost of such parts is quite high due to high-precision machining of the surface of finished products. The problem lies in the fact that during operation and storage, products are subjected to different climatic and operational influences and in many ways lose their production functions. The papers [1–5] report on studies on the possibility of extending the service life of non-ferrous metal products by periodic (or as necessary) physical and chemical treatment with specially created azeotropic mixture. These studies were carried out on high-precision copper mirrors of high-power CO₂ lasers [5], which during operation were subjected to various influences, that worsened their operational characteristics. The results obtained in this paper can be applicable for physical and chemical cleaning of such mirrors and other high-precision parts from non-ferrous metals.

This article is an integral part of the works cycle and is devoted to the creation of aerosol detergent compositions, designed for use during the operation of mirrors. In addition to high-precision copper mirrors, optical elements made of other materials were also studied in the work (see table 1).
The creation of a highly effective washing medium for carrying out the physical and chemical process of cleaning metal mirrors is fraught with considerable difficulties. The difficulties are as follows:

1) interaction of halogen-substituted hydrocarbons with alcohols, the presence of which is necessary to ensure highly efficient cleaning of metal mirrors (according to the results of previous studies on the removal of the main types of technological contaminations [1–5]);

2) instability of complex detergent compositions of the components with significantly different physical and chemical properties [6]. This occurs as the result of their different, often low, mutual solubility in each other and in the mixture and, as a result, their delamination over time, leading to a change in the physical and chemical properties of the respective cleaning compositions.

Complex detergent compositions usually do not create an azeotrope, and it is advisable to use them in aerosol containers. Wherein the following advantages are achieved:

a) keeping the physical and chemical properties of the cleaning composition for a long time by preventing its delamination into its component parts by increasing the mutual solubility of the components at the overpressure created by the propellant in the aerosol container;

b) using in the process of physical and chemical cleaning of metal mirrors not only the dissolving ability of the detergent composition, but also the impact force of its jet;

c) carrying out high-quality and easy-to-use cleaning of metal mirrors of various sizes and shapes, including in practical use, without dismantling them.

In light of the foregoing, in the present work experiments on cleaning high-precision metal mirrors and optical elements from other materials with detergent compositions in aerosol containers were carried out.

2. Experimental technique
The experimental technique was as follows.

The detergent composition was an azeotropic mixture of “Freon-114B2 (50% vol.) – methylene chloride (20% vol.) - ethanol (22% vol.) - acetone (8% vol.)” and had a solubility parameter \( \delta = 19.0 \) \( J^{1/2} \) cm\(^{3/2} \). It was placed into aerosol container. For the specified solvents, liquids of either "special purity" brand, or after preliminary rectification purification were used. Based on previous studies, the following recipe of the detergent composition for use in aerosol container was selected: detergent composition – 70% by weight; propellant (a mixture of gaseous Freon-11 and Freon-12 in a ratio of 1:1) - 30% by weight.

Before the cleaning process of the optical elements, the coefficient of specular reflection at a wavelength of 10.6 \( \mu \)m was measured in them. From the data of ellipsometric measurements at a wavelength of 0.63 \( \mu \)m, the optical characteristics (n, k, \( R_{0.63} \)) of the surface were calculated. We controlled (indirectly) the chemical purity of the optical surface on an electron fluorometer “EF-3MA”, as well as the geometric shape (N, \( \Delta N \)) of the optical surface and its optical purity (P).

The cleaning of optical elements was carried out by aerosol spraying until the optical surface was completely coated with the detergent composition. During a single treatment of the optical surface to form a continuous film, the consumption of the detergent composition was \( \approx 4 \) ml/cm\(^2\). The number of optical surface treatments with the azeotropic detergent composition “Freon-114B2 (50% vol.) – methylene chloride (20% vol.) – ethanol (22% vol.) – acetone (8% vol.)” was 3 processes, that is due to the analysis of the cleaning rate when using azeotropic detergent compositions carried out earlier [4].

3. Result and discussion
Measurement results of the values of optical constants and chemical purity of the optical elements are shown in table 1.

As it can be seen from the experimental results presented in table 1, reflection coefficient at a wavelength of 0.63 \( \mu \)m (\( R_{0.63} \)), calculated according to ellipsometric measurements, after cleaning using the detergent composition increased slightly compared to the reflection coefficient before cleaning for copper and alloys (except for steel 12X18H10T). For optical elements made of NaCl crystals, the reflection coefficient at a wavelength of 0.63 \( \mu \)m (\( R_{0.63} \)) remained unchanged.
Table 1. The values of optical constants and chemical purity.

| Samples, No. | Ellipsometric method | The amount of contaminations on the optical surface, g/cm² |
|--------------|----------------------|--------------------------------------------------------|
|              | before cleaning with the composition | after cleaning with the composition | before cleaning | after cleaning |
|              | n, k, R₀,63, %       | n, k, R₀,63, %                                       |                |              |
| No. 2 (aluminium and magnesium (6 %) alloy) | 0.68, 2.42, 69.1 | 0.81, 3.31, 77.1 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 3 (bronze (96 %) and zirconium (1 %) alloy) | 0.90, 3.05, 72.2 | 0.89, 3.30, 76.2 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 7 (bronze (96 %) and zirconium (1 %) alloy) | 0.89, 2.95, 71.3 | 0.91, 3.40, 76.0 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 10 (NaCl) | 1.52, 0.07, 4.3 | 1.52, 0.005, 4.3 | 1 × 10⁻³ | 1 × 10⁻⁶ |
| No. 21 (NaCl) | 1.48, 0.05, 3.8 | 1.48, 0.002, 3.8 | 1 × 10⁻³ | 1 × 10⁻⁶ |
| No. 31 (molybdenum) | 0.49, 1.24, 47.8 | 0.52, 1.32, 48.9 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 31 (steel 12X18H10T) | 0.77, 2.03, 57.3 | 0.79, 2.08, 53.1 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 110041 (Cu) | 0.14, 2.50, 93.0 | 0.16, 2.90, 93.4 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 416011 (Cu) | 0.13, 2.49, 93.0 | 0.15, 2.80, 93.5 | 1 × 10⁻³ | 1 × 10⁻⁷ |
| No. 416018 (Cu) | 0.14, 2.50, 93.0 | 0.12, 2.70, 94.0 | 1 × 10⁻³ | 1 × 10⁻⁷ |

Note. Other parameters did not change, in particular, the specular reflection coefficient at a wavelength of 10.6 μm remained unchanged (within the measurement accuracy - R[10.6] = ± 0.5). The reflection coefficient at a wavelength of 0.63 μm was calculated by the formula:

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

where \( n \) - is the refractive index of the sample material, \( k \) - is the absorption coefficient of the sample material.

The control of the chemical purity of the optical surface showed that the amount of contaminations on it significantly decreased after the cleaning process (for metals and alloys – by 4 orders of magnitude, for crystals – by 3 orders of magnitude).

However, the process of long storage of the detergent composition in aerosol container showed significant disadvantages in the application of this method. In particular, in aerosol containers made of aluminum and tin-plate, the material of this containers under certain conditions (elevated temperature, long storage) reacts with the products of the interaction of halogen-substituted hydrocarbons with other components of the detergent composition according to the equations [1]:

\[ \text{CCl}_3F_2 + H_2O \rightarrow CO_2 + 2HCl + 2HF \]

\[ \text{CCl}_3F + CH_2CH_2OH \rightarrow \text{CHCl}_2F + CH_3CHO + HCl \]

Moreover, in both cases, treatment with an "aged" composition in aerosol container leads to corrosion of the optical surface of the mirrors. The components of the cleaning composition themselves can dissolve the lacquer used to protect the aerosol container material from corrosion, or a rubber gasket connecting the container with the spray head. In the paper [7] the effect of methylene chloride on the corrosion of aerosol containers in the presence of water in a mixture with a propellant (dichlorodifluoromethane) and a solvent (ethanol) was evaluated. Also, in the presence of stabilizing additives in a detergent composition such as 2-methylfuran with epoxbytane (4 g/l) the seam of the aerosol package is etched, and a slight corrosive effect is exerted on the cylinder. This raises serious doubts about the advisability of using detergent compositions of such compound in aerosol containers.

From the results given in the paper [7], it is obvious that the main direction for stabilizing of detergent compositions in aerosol containers used for cleaning metal mirrors is the rejection of aluminum packages. Also it is necessary to refuse the protection of the inner surfaces of the containers with lacquer,
which protects them from the corrosive effects of the detergent composition. In addition, it is necessary to remove from the composition water and halogen hydracids that catalyze the corrosion process and the interaction of the components with each other.

As it was shown by the research results [1, 6, 9–14], that the optimal stabilizer of the cleaning composition in aerosol container for cleaning metal mirrors may be anionite AB-17*8 in hydroxyl form. It sorb water [11, 12, 15], which present in components at the level of solubility, and halogen hydracids. What is more, the presence of water promotes superequivalent absorption of acids [6].

In this regard, experiments were conducted to stabilize the detergent composition in aerosol container using anionite AB-17*8 in hydroxyl form.

The experimental procedure is as follows. The studies were carried out according to the method of accelerated testing in a heat chamber TPV-1000 at a temperature of 50 °C for 1 month and at room temperature for 6 months. For testing, the detergent composition “freon-114B2 (50% vol.) – methylene chloride (20% vol.) – ethanol (22% vol.) – acetone (8% vol.)” was placed in standard aerosol containers made of aluminum and tin-plate, as well as in glass ampoules. In all aerosol containers, except for the control containers, anionite AB-17*8 was placed in the amount of 3 g per 180 ml of the detergent composition. A mixture of gaseous freon-11 and freon-12 in the ratio “1:1 (% by weight)” and carbon dioxide was used as a propellant in aerosol containers. The test results are presented in table 2.

The test results presented in table 2 showed that the failure of metal containers occurs in all experiments, most intensively at elevated temperatures. The use of carbon dioxide as propellant and anionite AB-17*8 as a stabilizer for the detergent composition allows to reduce by an order of magnitude corrosion of aerosol containers at a temperature of 50 °C (examples 7, 12). And at room temperature the safety of aerosol containers made from tin-plate is guaranteed for 6 months. Among the stability of aerosol container materials, tin-plate has some advantage over aluminum and glass over tin-plate. But, as the test results showed, even the use of anionite AB-17*8 and carbon dioxide as a propellant does not guarantee the destruction of aerosol tin-plate containers at elevated temperatures and a changes in the physical and chemical properties of the detergent composition at room temperature. An analysis of the samples of the detergent composition in aerosol containers destroyed during testing was carried out. Only in glass ampoules (examples 10, 11) there was no corrosion of aerosol containers.

The most probable is the presence of F-, Cl- ions formed as a result of the decomposition of methylene chloride and freons [16, 17]. A qualitative reaction to F- ions is the interaction with CaCl₂ with the formation of a white precipitate:

\[ \text{Ca}^{2+} + 2\text{F}^- = \text{CaF}_2 \downarrow \]

All compositions, except for examples 10 and 11, gave a white colloidal precipitate. For the composition in the aerosol container made of tin-plate, qualitative reactions to iron ions as a result of corrosion of tin-plate under the action of F-, Cl- ions were carried out. When interacting with alkalis, Fe³⁺ gives a dirty green precipitate of Fe(OH)₃:

\[ \text{Fe}^{3+} + 2\text{OH}^- = \text{Fe(OH)}_3 \downarrow \]

This was observed in the compositions according to examples 5-8, 12 and 13. A qualitative reaction to Fe³⁺ is the interaction with potassium ferrocyanite, herewith bright blue staining is observed:

\[ 4\text{Fe}^{3+} + \text{Fe(CN)}_6 = \text{Fe}_{2}\text{Fe(CN)}_6 \downarrow \]

For the compositions of examples 5-7 and 12 the formation of a small amount of blue precipitate was observed.

Analysis of the compositions in aluminum aerosol containers for the presence of aluminum ions by the addition of KOH alkaline solution did not show precipitation of Al(OH)₃. The absence of Al³⁺-ions probably indicates that they react with F⁻-ions to form a soluble AlF₃ precipitate.

**Table 2.** Stability of aerosol containers depending on the material of aerosol containers, storage conditions and the presence of a stabilizer.

| Aerosol containers material, No. example and quantity | Storage conditions | Propellant | No of failed | Presence of anionite | Note |
|------------------------------------------------------|--------------------|------------|--------------|---------------------|------|
|                                                       |                    |            |              |                     |      |
### aerosol containers

|   | Alumnum (60 packs) | Room temperature | Mixture of freons |室 | - | Failure after 7 days |
|---|-------------------|------------------|------------------|---|---|---------------------|
| 1 |                   | 50 °C             | 36               |   |   |                     |
| 2 | Aluminum (60 packs) | 50 °C             | Mixture of freons | 60 |   | Anionite AB-17*8     |
| 3 | Aluminum (60 packs) | Room temperature | Mixture of freons | 60 |   | Anionite AB-17*8     |
| 4 | Aluminum (60 packs) | Room temperature | Mixture of freons | 31 |   |                     |
| 5 | Tin-plate (60 packs) | Room temperature | Mixture of freons | 30 |   |                     |
| 6 | Tin-plate (60 packs) | Room temperature | Carbon dioxide    | 24 |   |                     |
| 7 | Tin-plate (60 packs) | 50 °C             | Mixture of freons | 60 |   | Failure after 10 days |
| 8 | Tin-plate (60 packs) | 50 °C             | Mixture of freons | 37 | Anionite AB-17*8     |
| 9 | Glass (60 packs)   | 50 °C             | -                | -  | -  | Presence of a white precipitate in the detergent composition |
| 10| Glass (60 packs)   | 50 °C             | -                | -  | Anionite AB-17*8     |
| 11| Glass (60 packs)   | Room temperature  | -                | -  | Anionite AB-17*8     |
| 12| Tin-plate (60 packs) | 50 °C             | Carbon dioxide   | 15 | Anionite AB-17*8     |
| 13| Tin-plate (60 packs) | Room temperature | Carbon dioxide   | -  | Anionite AB-17*8     |

All compositions in metal aerosol containers obtain a slightly lemon color. Probably, this coloring gives a protective lacquer, which forms colored radicals upon decomposition.

Analysis of the detergent composition, placed into glass ampoules (examples 10, 11), according to the transmission spectra on spectrophotometer Hitachi-330 in the wavelength region of 300-700 nm showed the absence of dissolution of the anionite AB-17*8 in the cleaning composition. Registered transmission spectra of pure solvents and with anionite AB-17*8 practically do not differ.

### 4. Conclusion

The following conclusions can be made, based on the foregoing:

1. When aluminum and tin-plate aerosol containers are used, compositions that are used to clean metal mirrors should not contain chlorine-substituted hydrocarbons or even “traces” of water and hydroxyl ions. These are, for example, individual solvents such as ethanol, acetone or stable detergent compositions such as “freon-114B2 – acetone” azeotrope.

2. The use of the detergent composition “Freon-114B2 – methylene chloride – ethanol – acetone” is advisable only in freshly prepared form and in aerosol containers, that are resistant to the cleaning composition, such as glass, fluoroplast, nickel, steel, in the presence of anionite AB-17*8 in hydroxyl form as a stabilizer and carbon dioxide as a propellant.
3. The use of lacquer for protection against corrosion containers is inexpedient, since in the presence of the detergent composition it is dissolved, which leads to a change in the physical and chemical properties of the cleaning composition.

4. The use of a freshly prepared azeotrope detergent composition “freon-114B2 – methylene chloride – ethanol – acetone” allows to reduce the amount of technological contaminations, that are present on the optical surface by 3-4 orders of magnitude, with a slight increase in the reflection coefficient at a wavelength of 0.63 μm (R_{0.63}) and with keeping the rest parameters.

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