Regeneration and utilization of solvents after the process of physical and chemical cleaning of metal optics

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Abstract. The possibility of application of a semipermeable polymer membrane in total with the method of rectification purification for the repeated use of freon-114B² and detergent compositions based on it for cleaning metal optics in a closed technological cycle while ensuring the environmental cleanliness of the process and saving solvents has been identified and justified. The investigated adsorption method is effective for cleaning freon-114B² from rosin resins contaminants: among adsorbents (activated carbon, silica gel, anion exchange resin IA-I, silica gel S-80). Silica gel S-80 has the highest adsorption capacity (up to 50 mg / l). It has been shown that regeneration of freon-114B² with the help of a polymer semipermeable membrane after its use for cleaning metal optics allows to reduce the amount of impurities present in it by at least 2 orders of magnitude. Moreover, organic molecules, that have long surfactant chains, oils, fats of organic and mineral origin are almost completely separated from the regenerated solvent.

1. Introduction

For the operation of high-power CO₂ lasers, metallic mirrors are used [1]. They are – a high-precision, expensive products, the working optical surface of which must be operated in the most pure state. The presence of traces of the polishing process and operational contaminants on the surface leads to the degradation of the mirror. To clean the surface of the mirror organic solvents with the brand "especially pure" are used. However, for implementation of the physico-chemical process for cleaning of metal optics in the semi-industrial variant, one, even optimal, choice of washing medium is not enough. It is necessary to organize a closed technological process of purification, including the development of a method for the regeneration of spent solvents (using each time a new portion of expensive solvents for cleaning and disposal, including the environmental factor, involves significant costs). This work is devoted to the study of the process of regeneration of the main component in the compositions used for cleaning metal optics. This is the purification of freon-114B² from technological impurities, which pass into the solvent after the process of cleaning metal optics.

The regeneration of spent solvents is similar to the method of purification of solvents before their use and is usually carried out by the method of rectification. However, in the process of regeneration, it is necessary to remove significant amounts of washed contaminants. When using this method, this can lead to a rapid failure of distillation columns due to the accumulation of significant amounts of contaminants in them and the need for their frequent cleaning, which requires significant costs.
Therefore, in [2, 3], an adsorption purification method is used to regenerate solvents, which complements the distillation purification (at the preliminary stage), and in some cases replaces it. This method is implemented by passing contaminated freons in a condensed form through a layer of highly effective adsorbent: $\text{Al}_2\text{O}_3$, $\text{SiO}_2$, coal zeolites with slit pores $\sim 5$ Å, and zeoline are commonly used. Wherein the water content decreases to $1 \cdot 10^{-6}$% by weight, and the decomposition temperature of freons increases accordingly. The disadvantages of the method are: 1) low degree of purification of freon at low productivity (5 kg of pure freon per hour), bulkiness and complexity of equipment during exploitation; 2) when using molecular sieves, activated carbon, aluminum gel, etc. as adsorbents, mainly low molecular weight impurities such as water are removed from solvents (one of the most effective adsorbents for its extraction are synthetic zeolites). In the manufacture of solvents brand "especially pure" the use of this method is possible only in combination with the method of distillation purification, since they may be contaminated with adsorbent material in particular, with anion exchanger AB-17-8 [3]. Therefore, the experiments on the regeneration of freon-$114B_2$ were carried out in two stages: 1) removal of rosin and surface-active substances (surfactants) by the adsorption method; 2) distillation purification. Rosin is widely used for the manufacture of polishing pads, and surfactant is a part of the liquid used in the optical processing of metal optics [4]. Using of rosin as model contamination is due to its predominant presence in the impurities that are washed with solvents and the use of surfactants - the difficulty of removal during regeneration compared with other impurities [5, 6].

A characteristic feature of surfactants is the tendency to micelle formation at concentrations exceeding the critical concentration. Most of the studied surfactant adsorption region is the region of the existence of micellar structures, as a result of which the adsorption isotherms of the surfactant are complex [6]. Under dynamic conditions, the capacity of anion exchanger for surfactants depends on the presence of mineral ions (in their absence, the appearance of surfactants (“overshoot”) is observed already in the first portions of the filtrate), the transmission rate of the solution and its concentration. Moreover, at a concentration equal to critical concentration, the adsorption capacity, for example, of cation exchanger KU-2-8, falls. This is probably due to the presence of micelles in the solution, the adsorption of which is difficult.

Techniques for the quantitative determination of various types of surfactants in aqueous solutions are described in [6]. To determine the free surfactant molecules in non-aqueous solutions, the characteristic bands of the spectra related to the stretching vibrations of the bonds of the polar groups of the surfactant molecules are used (the association of surfactant molecules in non-polar liquids, as a rule, is realized through the interaction of these groups).

2. Experimental technique

As model solutions in the experiments, we used 0.01–0.4 % weight. rosin and 0.01–0.5 % weight. sulfanol surfactant (anionic surfactant, a mixture of isomers of sodium salts) in freon-$114B_2$ (due to its maximum content compared with other components in the selected detergent composition). The range of concentrations of contaminants in the model solution is due to the amount of impurities actually present in the solvents before the regeneration process. As adsorbents, activated carbon, silica gel, anion-exchange resin IA-1, $S$-30 silica gel, a strong base cation exchanger KU-2-8 in the hydrogen form and a strong base anion exchanger JRA-401 in the hydroxyl form were chosen. The use of anion exchangers and cation exchangers is caused by the fact that adsorbents like activated carbon and silica gel absorb mainly low molecular weight impurities and practically do not absorb surfactants [2, 7].

The technique of conducting experiments on adsorption of rosin and surfactant from a solution of freon-$114B_2$ under dynamic conditions is as follows. A suspension of the adsorbent in freon-$114B_2$ was loaded into a column with a diameter of 11 mm and a height of the absorbing layer of 9 and 15 cm. Since the density of the solvent is higher than that of the solid phase, the adsorbent floated to the surface. The excess solvent was removed from the bottom of the column, and then the adsorbent layer was pressed to the bottom filter with a glass wool swab. Then a model solution was supplied. To determine the content of rosin in freon-$114B_2$, the dependence of the optical density of solutions on the concentration of the dissolved substance was used. The determination of abietic acid (which form the
main mass of rosin) concentrations, is usually carried out by absorption bands (\(\lambda\)) – 232, 240 and 250 nm [7]. Considering the significant absorption of freon-114B2 in the mid-UV region of the spectrum, \(\lambda = 340\) nm was used. According to the results of measurements on the SF-4A spectrophotometer, a calibration straight line was built (figure 1), which was later used to determine the concentration of the solution passed through the column (reference solution — 114\(B^2\) Freon — "especially pure").

The concentration of surfactant in freon-114\(B^2\) was determined as follows: an aliquot (15 ml) of the surfactant solution in freon-114\(B^2\) was placed in a separatory funnel and 25 ml of distilled water was fed into it. The solution was kept for 5–7 minutes. During this time, a portion of the surfactant was extracted into the aqueous phase. After that, the optical density of the obtained aqueous solution was measured on an SF-4A spectrophotometer at \(\lambda = 260\) nm. This technique has a sensitivity allowing detecting the presence of surfactant in the solution leaving the column at a concentration of up to 10–6 % weight.

3. Results and discussion

The test results on adsorption of rosin from freon-114\(B^2\) solution in columns are presented in figure 2. It is shown, that when using activated carbon, silica gel and anion-exchange resin IA-1 (curves 1, 2, 3) as adsorbents, the adsorption of rosin from the freon solution is practically absent, the rosin appears in the first portions of the solvent. Silica gel \(S\)-80 well absorbs rosin from freon-114\(B^2\), and the absorption value increases with increasing amount of adsorbent in the column (curves 4, 5). The adsorption capacity of silica gel \(S\)-80, determined from curve 5, is 50 mg/l. When passing surfactant solutions in freon-114\(B^2\) through columns with adsorbents (silica gel \(S\)-80, activated carbon, cation exchanger KU-2x2 in hydrogen form and anion-exchanger \(JRA\)-401 in hydroxyl form), the presence of surfactant was detected in the first portions leaving the solution columns.

When passing through the column with silica gel \(S\)-80, which absorbs rosin well, a solution of freon-114\(B^2\) with a rosin content of 0.1 % wt. and trace amounts (0.005 % wt. surfactant) absorption of rosin was absent. That is, studies have shown the ineffectiveness of the adsorption method of regeneration of freon-114\(B^2\) from technological contaminations in the presence of surfactants (surfactants are not removed from the solvent, also preventing the removal of rosin).
Therefore, experiments on freon regeneration were carried out using the filtration method through semipermeable polymeric membranes [8]. The advantage of this method is a rather high quality of solvent cleaning and higher productivity than with the adsorption method with minimal energy costs. A significant defect of the method is the lack of universalism: the selectivity of polymer membranes requires the use of a membrane with a specific pore size for a particular type of solvent.

The experimental procedure was as follows. As a material for the manufacture of the membrane, a film of polyethylene terephthalate (PET) with a thickness of 50 mkm (Industry standard 4.023.001-73) was used as the most resistant to freon type solvents. To give this film the maximum defect structure and properties of the polymer membrane against freon-114\(B_2\), it was pre-soaked for 2 hours in a water-acetone binary solution (43–47% by volume of acetone) with a solubility parameter \(\delta = 33.6 \text{ J}^{1/2} \text{ cm}^{-3/2}\).

The choice of this solution for modify the structure of the film is due to the ability of liquids with similar solubility parameters \(\delta\) to amorphous-crystalline polymers like PET to change the structure of the latter due to crystallization processes. The latter proceed so intensely that the film loses its mechanical strength and is not suitable for further use (significant swelling and partial or complete dissolution of the polymer occur). The intensity of crystallization can be reduced by adding a liquid into the system, which also participates in the formation of the polymer structure, but with a solubility parameter \(\delta\), which is significantly different from the solubility parameter \(\delta\) of the polymer. It is water that is the specific component in the presence of which in the system "PET (\(\delta = 21.9 \text{ J}^{1/2} \text{ cm}^{-3/2}\)) – water (\(\delta = 47.8 \text{ J}^{1/2} \text{ cm}^{-3/2}\)) – acetone (\(\delta = 19.3 \text{ J}^{1/2} \text{ cm}^{-3/2}\))" a defective porous structure is formed in the polymer.

The exposure time of the PET film in the solution was determined by the time it takes to reach an equilibrium degree of swelling, which is set in a water-acetone solution after 2 h. Similar results on the creation of a defective structure of a PET film gives it processing in a binary solution “water – dioxane” with a solubility parameter \(\delta = 47.5 \text{ J}^{1/2} \text{ cm}^{-3/2}\) with a dioxane content of 23–27% by volume.

To study the rate of regeneration of freon-114\(B_2\) we used equipment that includes a mixer for mixing the contaminated solvent; nitrogen trap; a thermostatted separation cell, the case of which consists of two parts, between which a polymer membrane with a working area of 19.2 cm\(^2\) is fixed; backing pump. The principle of its operation is as follows. Before the start of the experiment, the space under the membrane is pumped out with a backing pump to a pressure not exceeding 10 Pa during the experiment. As a model mixture, a solution of freon-114\(B_2\) with rosin (0.1–0.3 % wt.) and a surfactant of the sulfanol type (0.1 % wt.) were used. This mixture was poured into the upper part of the separation cell. Under the action of pressure drop and its own gravity, it selectively seeped through the pores of the polymer membrane, freeing itself from the bulk of contaminants that are larger than the pores.

The value of the mixture flux density which passed through the polymer membrane over a certain period of time was determined by weighing the amount of the mixture passed. The composition of the mixture was measured on an SF-4A spectrophotometer at \(\lambda = 340\) nm. The degree of structure defectiveness of the PET film after treatment in binary solutions was determined by IR spectra. The results of the study of the PET membrane modified in binary solutions, degree of defectiveness, the density of the past flow and the concentration of rosin in the model solution before and after passing through the membrane are presented in table 1.
from optimal (25 % vol) and acetone to 2 % vol from the optimal (45 % vol), the achieved degree of imperfection of the structure of the PET film decreases and, accordingly, decreases the density of the flow.

**Table 1.** The dependence of the density of the past flow, the concentration of rosin, the degree of defectiveness.

| The method of modification of PET film | Binary solution concentration, % wt | Density of flow, 10³ kg/m²h | Concentration of rosin, % wt. | Degree of defectiveness, % |
|--------------------------------------|-------------------------------------|----------------------------|-------------------------------|-----------------------------|
| Amorphous PET                        | Pure freon 114B2                    | Model mixture of rosin in freon-114B2 | Original model mixture of rosin in freon-114B2 | Model mixture after filtration | Degree of defectiveness, % |
| Treated with "dioxane-water" solution | On the one hand                     | 25                          | 14                           | 2                            | 0.3                         | 0                           | 1–2                         |
|                                      |                                    | 23                          | 5000                         | 40                           | 0.3                         | 0.1                         | 29                         |
|                                      | From two sides                      | 25                          | 1000                         | 90                           | 0.3                         | 0.1                         | 33                         |
|                                      |                                    | 25                          | 6000                         | 40                           | 0.3                         | 0.1                         | 33                         |
|                                      |                                    | 27                          | 4800                         | 30                           | 0.3                         | 0.1                         | 24                         |
| Treated with "acetone-water" solution | On the one hand                     | 45                          | 300                          | 10                           | 0.3                         | 0                           | 7                          |
|                                      |                                    | 43                          | 1400                         | 100                          | 0.2                         | 0.03                        | 25                         |
|                                      | From two sides                      | 45                          | 1800                         | 120                          | 0.1                         | 0.03                        | 33                         |
|                                      |                                    | 47                          | 1350                         | 95                           | 0.3                         | 0.03                        | 24                         |

This is probably due to the fact that when the composition of a binary solution deviates from the optimum, its solubility parameter (λ) changes and, thus, an optimal defect structure of the PET film is not achieved. In this case, predominantly pores with a diameter not exceeding 20 Å are formed in the film, through which freon-114B2 (the size of molecules of which is 18 Å) can leak out, being freed from the main mass of contaminants having dimensions of molecules larger than 20 Å. These are mainly molecules of surfactant, fats and oils of organic and animal origin. The contaminants retained by polymer membrane together with the membrane itself are subsequently utilized.

**Recommendation.** Regeneration of freon-114B2 and detergent compositions based on it by means of a polymer membrane should be carried out when organizing a closed technological cycle of the physico-chemical process of cleaning metal optics before final purification of solvents by the method of rectification.

**4. Conclusion**

1. The adsorption method is effective for cleaning freon-114B2 from contamination with rosin resins. Among of adsorbents (activated carbon, silica gel, anion exchanger IA-I, silica gel S-80), silica gel S-80 has the highest adsorption capacity (up to 50 mg/l). It has been established that the use of silica gel S-80, activated carbon, cation exchanger KU-2*2 and anion exchanger JRA-401 is not effective when cleaning freon-114B2 from surfactants and mixtures of rosin with surfactants. The mechanism of this effect apparently consists in the fact that, at concentrations exceeding critical concentration, large agglomerates are formed in aqueous solutions of surfactants, the adsorption of which is difficult. In non-polar organic liquids, a gradual association of surfactant molecules occurs, and the concentrations at which this process begins may be significantly lower than the critical concentration for aqueous solutions [9].

2. Regeneration of freon-114B2 with the help of a polymeric PET membranes after using them to clean metal optics allows reduce the amount of impurities present in it by at least 2 orders of magnitude, and organic molecules with long chains of surfactant type, oils, fats of organic and mineral origin are
separated from the regenerated solvent almost completely. A probable mechanism of this phenomenon is proposed.

3. The use of filtration and distillation purification methods in total allows to reuse the detergent compositions on the basis of freon-114B2 for cleaning metal optics in a closed technological cycle, ensuring the environmental friendliness of the process and saving of solvents. The need for pre-treatment is dictated by its advantages: high throughput, low energy intensity and the ability to quickly remove the filtrate and the membrane itself, which is made easily replaceable, and significant losses of solvents when using only the rectification method. Based on the above experimental results and recommendations based on them, the process of physico-chemical cleaning of metal optics was implemented technically.

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