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Corresponding Member of the USSR Academy of Sciences I. N. Plaksin, V. I. Solnyshkin,

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Abstract

Full Text

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Corresponding Member of the USSR Academy of Sciences I. N. Plaksin, V. I. Solnyshkin,
E. M. Chaplygina

THE ACTION OF OXYGEN ON OLEIC ACID

In the flotation of a number of sulfide and oxidized minerals, preliminary aeration of the pulp or of the flotation reagents has an effective action. Dissolution of atmospheric oxygen in the flotation pulp or oxygenation of reagents of the oxyhydryl collector type increases mineral recovery and promotes better separation ([1]-[5]).

A study of the interaction of oxygen with tridecylic acid when it is fixed on fluorite shows a noticeable increase in adsorption ([6]). It may be considered that the action of oxygen should be attributed to its influence on the acid group.

In the experimental work, the selected fatty acid was saturated with oxygen and nitrogen for various periods of time, and the peroxide compounds formed in this process were determined by the method of chemical analysis. Simultaneously, the absorption bands of the carboxyl groups and double bonds of oleic acid were studied in the infrared spectrum before and after treatment with oxygen. The results of determining the peroxide number of oleic acid treated with oxygen and then with nitrogen are given in Table 1.

Table 1

Peroxide number of oleic acid after treatment with oxygen and nitrogen

Duration of treatment, min.	Duration of treatment, min.	Peroxide number
O_2	N_2	
–	–	0.93
30	–	1.03
60	–	1.20
120	–	1.40
60	120	0.68
60	360	0.70
120	360	0.67

The infrared absorption bands were investigated in the regions 5–7 and 10–12 μ. Treated and untreated preparations were placed between two plates of sodium

Fig. 1

Figure 1: Fig. 1

chloride with windows of staniol 0.1 mm thick. The gap was adjusted with contour windows made of staniol 0.1 mm thick. Spectra were recorded on an IKS-12 instrument with a rock-salt prism, point by point.

To clarify the action of oxygen on the absorption band of the carboxyl group, samples were prepared from a solution of oleic acid in a mixture of medicinal vaseline oil with purified paraffin. The viscosity of the hydrocarbon solution was in the range 36–40 poise (according to Volarovich). The concentration of acid in the solution reached 0.5%, which made it possible to obtain the spectrum of the group under study with a reagent content on the plate of 0.045 mg/cm^2. The oil solution of the reagent was vigorously stirred while oxygen was bubbled through it. At definite time intervals, a sample was taken for recording spectrograms. The emulsion was prepared by adding water in amounts calculated from the weight of the volume being treated.

Figure 1 shows the spectra of a 0.5% solution (water content, 0.1%) during the passage of a stream of oxygen for 33 hours. As treatment proceeds, the band of the acid group decreases, and absorption appears in the spectrum [[unclear: sentence continues on next page]].

metric vibrations of carboxyl (1420 cm^{-1}). In an anhydrous solution this process is not observed. The absorption band at 1465 cm^{-1} is assigned to the hydrocarbon groups CH_2 of the fatty acid and of the medium.

Fig. 2 shows that, as the water content in the emulsion increases, the time required for disappearance of the absorption band at 1700 cm^{-1} decreases, which confirms the action of water molecules. A similar effect is obtained when hydrogen peroxide is added to the solution.

Fig. 1. Disappearance of the absorption band near 1700 cm^{-1} and development of symmetric vibrations of the carboxyl ion (1420 cm^{-1}) during treatment with oxygen of a solution of oleic acid in oil containing 0.1% water

Further study of the change in the spectrum of oleic acid was carried out in the 10–12 μ region, where the absorption bands of oxygen–carbon bonds are located. Since the absorption of the bands situated in this portion of the spectrum is of medium or low intensity, the method of preparing the specimens was changed for this case. An emulsion of oleic acid in water was treated with oxygen for 4 hours. The resulting finely dispersed mixture was allowed to settle, and the unreacted reagent was separated in a separatory funnel. From the aqueous emulsion the specimen was extracted with sulfur ether, after which the solvent was removed under vacuum at room temperature. The samples obtained were examined on a spectrometer with a fluororeagent layer thickness of 1.05 mm.

The spectrogram data are given in Fig. 3. On the untreated sample there

Fig. 2

Figure 2: Fig. 2

Figure 3. Absorption bands of oleic acid at a sample thickness of 1.05 mm before (1) and after (2) treatment of the aqueous emulsion with oxygen

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appear bands at 826 and 880 cm^{-1}, assigned to the epoxy groupings of oleic acid molecules and formed in the process of spontaneous dissolution of atmospheric oxygen (^{7}). The band at 928 cm^{-1} corresponds to absorption by COOH groups. As has been established, vibrations of the hydroxyl groups of amphoteric and basic compounds appear in this region of the spectrum (^{8}). Oleic acid possesses amphoteric properties to one degree or another.

Fig. 2. Decrease of the absorption band near 1700 cm^{-1} with supply of oxygen, depending on the water content in the emulsion: 1 –0.1%, 2 –0.2%, 3 –0.5%, 4 –0.8%, 5 –1.0%

In the oleic-acid preparation treated with oxygen, the band at 826 cm^{-1} does not change. The absorption at 885 cm^{-1} shifts toward higher frequencies, and the band at 938 cm^{-1} disappears. A new absorption band appears in the spectrum at 840 cm^{-1}, corresponding to peroxide groupings (^{8}). The absence in the spectrum of the treated preparation of the band at 938 cm^{-1} indicates that the formation of peroxide groups proceeds more readily in oleic acid molecules with amphoteric properties. Chemical-analysis data confirm that the appearance of peroxide group-

Fig. 3. Absorption bands of oleic acid at a sample thickness of 1.05 mm before (1) and after (2) treatment of the aqueous emulsion with oxygen.

is connected with epoxy groups, since after treatment with nitrogen the peroxide number falls by half. This indicates correspondence between the oxygen content in the chemical formulas of peroxides and epoxides.

Figure 4 gives a possible model of the structure of peroxide aggregates formed at the surface of particles. The peroxide groups stitch molecules together and form quasi-crystalline layers, which leads to an increase in the adsorption of certain oxhydryl flotation reagents.

Fig. 4. Model of the structure of a peroxide aggregate in the diffusion layer.

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A special feature of this model is that peroxide formation of polymolecular layers is only slightly sensitive to heavy-metal ions. The second factor is rupture of the double bond, its conversion into a single bond, and the transition of the cis-configuration of the molecules into a peroxystearic, straight chain. This frees the second half of the hydrocarbon chain from intramolecular bonds. To the peroxide groupings are added the van der Waals forces of the CH_2 groups, increasing the probability of formation of polymolecular layers. Treatment of the emulsion with nitrogen leads to destruction of the peroxide groupings.

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Note: Figure translations are in progress. See original paper for figures.