Mechanocomposites as New Materials for Solid-Phase Cosmetics

TATIANA F. GRIGORYEVA, IRINA A. VORSINA, ANTONINA P. BARINOVA and NIKOLAY Z. LYAKHOV

Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: grig@solid.nsk.su

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Abstract

The initial stages of mechanical activation of the layered silicates with higher alcohols and hydroxyacids are investigated by means of IR spectroscopy and X-ray phase analysis. The formation of new materials is established; they are dispersed layered mechanocomposites formed due to neutralization of the active centres of basic character on the silicate surface by the protons of carboxylic groups of hydroxyacids or hydroxyl groups of higher alcohols. Hydroxyl groups of acid do not participate in the reaction with silicates. They are likely to form hydrogen bonds both with hydroxyl groups of silicates and with water molecules formed during mechanical activation.

INTRODUCTION

Hydroxy acids are known to be widely used at present in cosmetics as exfoliants, which cause thinning of the corneal layer of skin, and as stimulators of cell metabolism accelerating their division; the activity of hydroxy acids is higher in the case when their concentration is higher. However, concentrations of these compounds in liquid-phase cosmetic materials are limited because of strongly acid solutions irritate skin. Solid-phase materials intended for solid-phase cosmetics could help overcoming these limitations; in addition, they can serve as daytime decorative and curative means of prolonged action. A new mechanochemical technology of the development of solid-phase materials in the form of mechanocomposites of layered silicates and hydroxy acids requires detailed investigation of mechanochemical interaction of these acids with kaolinite and talc, natural silicates which are often used in cosmetic preparations.

Investigations of the process of joint mechanical activation (MA) of layered silicates with organic acids (containing one and two carboxylic groups, and amino group) and inorganic ones [1, 2] showed that mechanochemical interaction between the components of mixture leads to neutralization of the surface active centres of basic character in silicate, which are formed during MA, by protons of acids. Active centres of acidic character, which are formed also during MA of silicate participate only in reactions with metal oxides having clearly exhibited basic properties [3].

Hydroxy acids include along with carboxylic groups also hydroxyl ones; a question arises whether hydroxyl groups participate in chemical interaction with silicates during mechanical activation of the systems containing these acids. Only a few works deal with mechanochemistry of organic acids. Among them, investigation of the optical isomeric effect under mechanochemical interaction of talc with hydroxyphenylacetic acid [4] and mechanochemical racemisation of *l*-leucine [5] should be noted.

In the present work we describe investigation of the formation of new forms of composite materials based on talc and kaolinite, containing hydroxy acids and higher alcohols, for the purpose of revealing the role of functional groups of these compounds in mechanochemical interaction with natural layered silicates.

EXPERIMENTAL

Kaolinite, Mg-talc, cetyl alcohol and three hydroxy acids – *l*(–)-tartaric, *dl*-tartaric (racemic acid) and citric – were involved in the investigation. Molar ratio of the components in silicate : alcohol mixture was 1 : 0.2, silicate : acid = 1 : 0.25, 1 : 1.

Mechanical activation was carried out in a ball mill of planetary type AGO-2 with the frequency of drums rotation around the common axis ~100 rpm and ball diameter 5 mm [6].

The IR absorption spectra were recorded with Specord-75IR spectrometer; samples were prepares as tablets with calcined KBr.

The X-ray diffraction investigation was carried out using URD-63 diffractometer with CuK_α radiation.

RESULTS AND DISCUSSION

Mechanical activation of a mixture of layered silicate with cetyl alcohol

Cetyl alcohol $C_{16}H_{23}OH$ (melting point 49.3 °C) in the solid-state forms polymer associates due to relatively strong hydrogen bonds, which is confirmed by the position of the band of stretching vibrations νOH in the IR spectrum (Fig. 1, *a*) 3450–3250 cm^{-1} [7]. The interval of νOH also provides evidence that the alcohol molecules are oriented along the maximal strength of hydrogen bonds characteristic of the crystalline state of the alcohol. The band with two maxima – 1475 and 1465 cm^{-1} – is assigned to the mixed vibrations δOH + δCH_2; the band at 1060 cm^{-1} relates to νC–O vibrations [7].

Mechanical activation of pure cetyl alcohol for 3 min does not cause any substantial changes in its structure: the IR spectra of the initial and activated (τ_a = 3 min) samples are almost identical. It is known that the destruction of structure in kaolinite and talc occurs under mechanical treatment very rapidly: after activation for 20 s, a sharp decrease in the intensities of all the diffraction peaks is observed; especially large changes occur with the reflections from the basal planes 001, 002 [8]. The X-ray diffraction investigations of the mixtures of kaolinite with cetyl alcohol showed that no substantial changes occurred with the diffraction reflections of kaolinite are observed after activation for 30 s, but the diffraction peaks of cetyl alcohol disappear almost completely (Fig. 2).

In the IR spectra of a mixture of kaolinite with cetyl alcohol, activated for 30 s, the character of absorption changes substantially within the regions 3600–3100 and 1500–1400 cm^{-1}, where the absorption bands of OH groups of the alcohol νOH and δOH manifest themselves. A weak band with a maximum at ~1630 cm^{-1} appears. In the 1500–1400 cm^{-1} range, one band with a maximum at 1470 cm^{-1} ($\delta_s CH_2$) and a shoulder at ~1455 cm^{-1} ($\delta_{as} CH_3$) appears [7]. The band is noticeably broadened. After activation of the sample for 3 min (see Fig. 1, *b*) this band somewhat broadens, the band with the maximum at 1630 becomes more clear, and a broad band with a maximum at 3430 appears in the region 3600–3100 cm^{-1}. The bands with maxima at 1630 and ~3430 cm^{-1} can be attributed to stretching and bending vibrations of water molecules, respectively [9]; their appearance can be evidence of the formation of molecular water during MA of a mixture of silicate with cetyl alcohol. One can also see in Fig. 1, *b* that the intensities of bands related to the stretching (3600 cm^{-1}) and bending (940 and 915 cm^{-1}) vibrations of OH groups of kaolinite decrease. No substantial changes are observed in the bands of the basic vibrations of tetrahedral and octahedral networks of kaolinite layer (regions 1150–950 and 800–700 cm^{-1}) [11, 12], only the intensity of maximum at 1115 cm^{-1} of the band related to antisymmetric stretching vibrations ν_{as}Si–O–Si. The data of XPA and IR spectroscopy provide evidence that the crystal structure of kaolinite is conserved in general.

Changes in the character of absorption in the region 3600–3100 cm^{-1}, a decrease in the intensity of the vibration bands of the surface and internal OH groups of kaolinite [12] with simultaneous changes in the band within

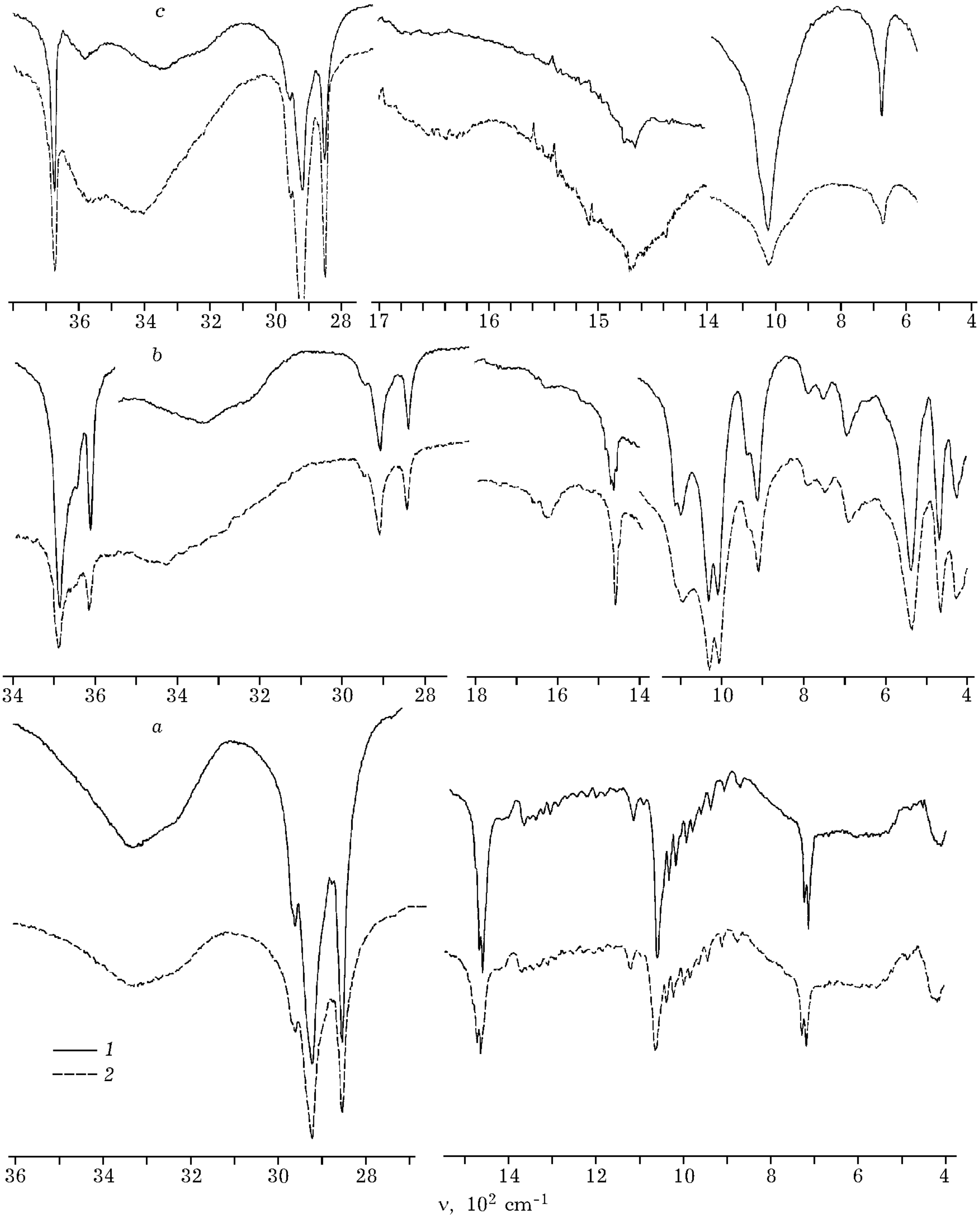

Fig. 1. IR absorption spectra of cetyl alcohol (*a*) and its mixtures with kaolinite (*b*) and with talc (*c*) before (*1*) and after activation for 3 min (*2*).

1500–1400 cm^{-1} and the appearance of OH vibrations of water molecules are likely to provide evidence of the mechanochemical interaction of cetyl alcohol with the basic centres of kaolinite, similarly to the interaction of kaolinite with organic acids [1, 2]. As a result, mechanocomposite is formed, in which the surface metal ions of silicate are chemically bound with the alkyl through the oxygen bridge, that is, the bond of the same type as that in alcoholate is formed.

The interaction in the system cetyl alcohol – Mg-talc during their joint MA proceeds more actively that in the system alcohol – kaolinite. As it follows from Fig. 1, *c*, the bands of hydroxo groups of the alcohol νOH (3450–

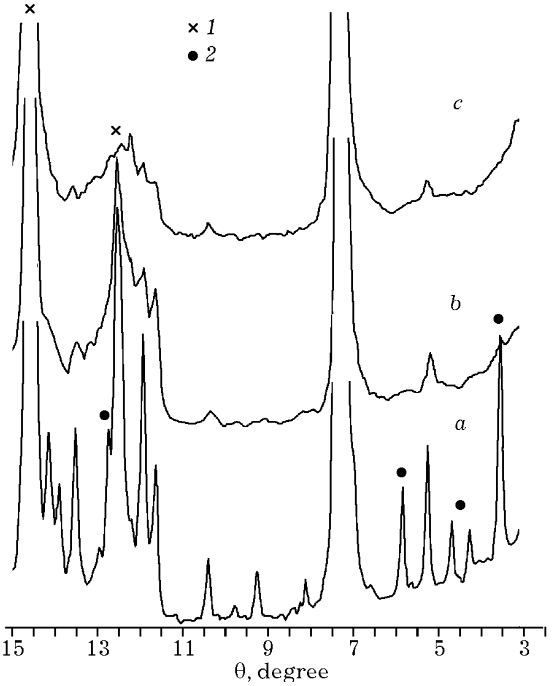

Fig. 2. X-ray diffraction patterns of the mixtures of cetyl alcohol with kaolinite before (*a*) and after activation for 30 s (*b*), 3 min (*c*): *1* – kaolinite, *2* – cetyl alcohol.

3250 cm^{-1}) and δOH (1500–1400 cm^{-1}) are almost absent from the IR spectra of the mixture activated for 3 min. By this moment of activation, the intensity of νOH bands of hydroxo groups of talc (3675 cm^{-1}) decreases; characteristic bands of molecular water (~3430 and ~1630 cm^{-1}) appear [9]. The observed changes in the bands of IR spectra of the activated mixtures of cetyl alcohol with talc also provide evidence of the mechanochemical interaction in this system according to the scheme similar to that for the system kaolinite – cetyl alcohol.

As a result of investigations, it was established that the hydroxo groups of higher alcohols are able to enter chemical reactions with the surface groups of natural silicates.

Mechanical activation of the mixtures of layered silicates with hydroxy acids

Dihydroxy acids *l*(–)-tartaric and *dl*-tartaric (racemic) acids, similarly to triacid – citric acid, form associates [7, 10] and form chains composed of the molecules lying in one plane and bound to each other with strong hydrogen bonds. Mechanical activation of the initial acids does not lead to substantial changes in their structure; the IR spectra of the acids before activation and after it are almost identical (Fig. 3).

It was established above that the mechanochemical interaction in the system layered silicate – higher saturated alcohol occurs due to neutralization of the active base centres of the silicate by the protons of hydroxo groups of an alcohol. Because of this, it may be expected that the mechanochemical reaction during MA of layered silicates with hydroxy acids will be participated with not only by the protons of carboxylic groups but also by the protons of hydroxyl groups.

It follows from the comparison of the IR spectra of the activated mixtures silicate – tartaric acid and silicate – racemic acid that there are no differences in the character of interaction at the initial stages of MA in these

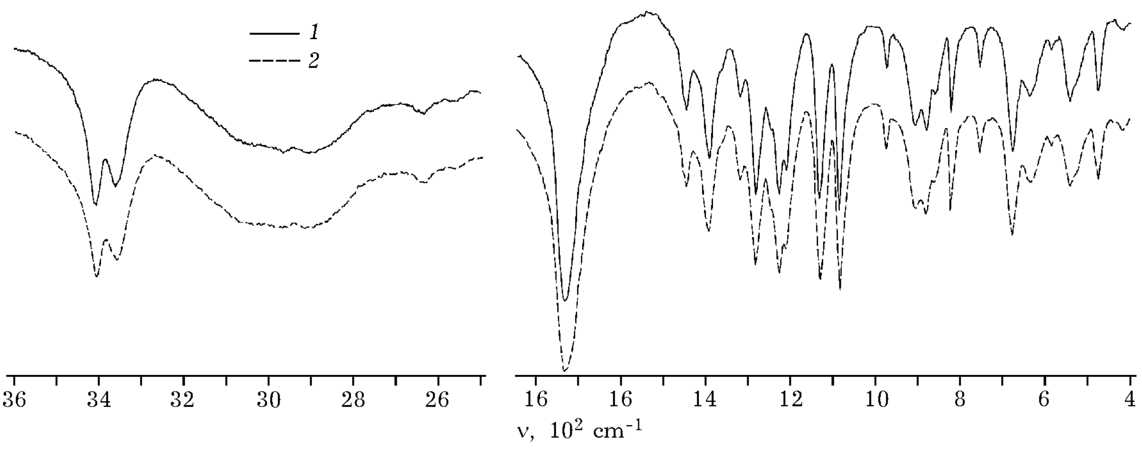

Fig. 3. IR absorption spectra of racemic acid before (*1*) and after activation for 10 min (*2*).

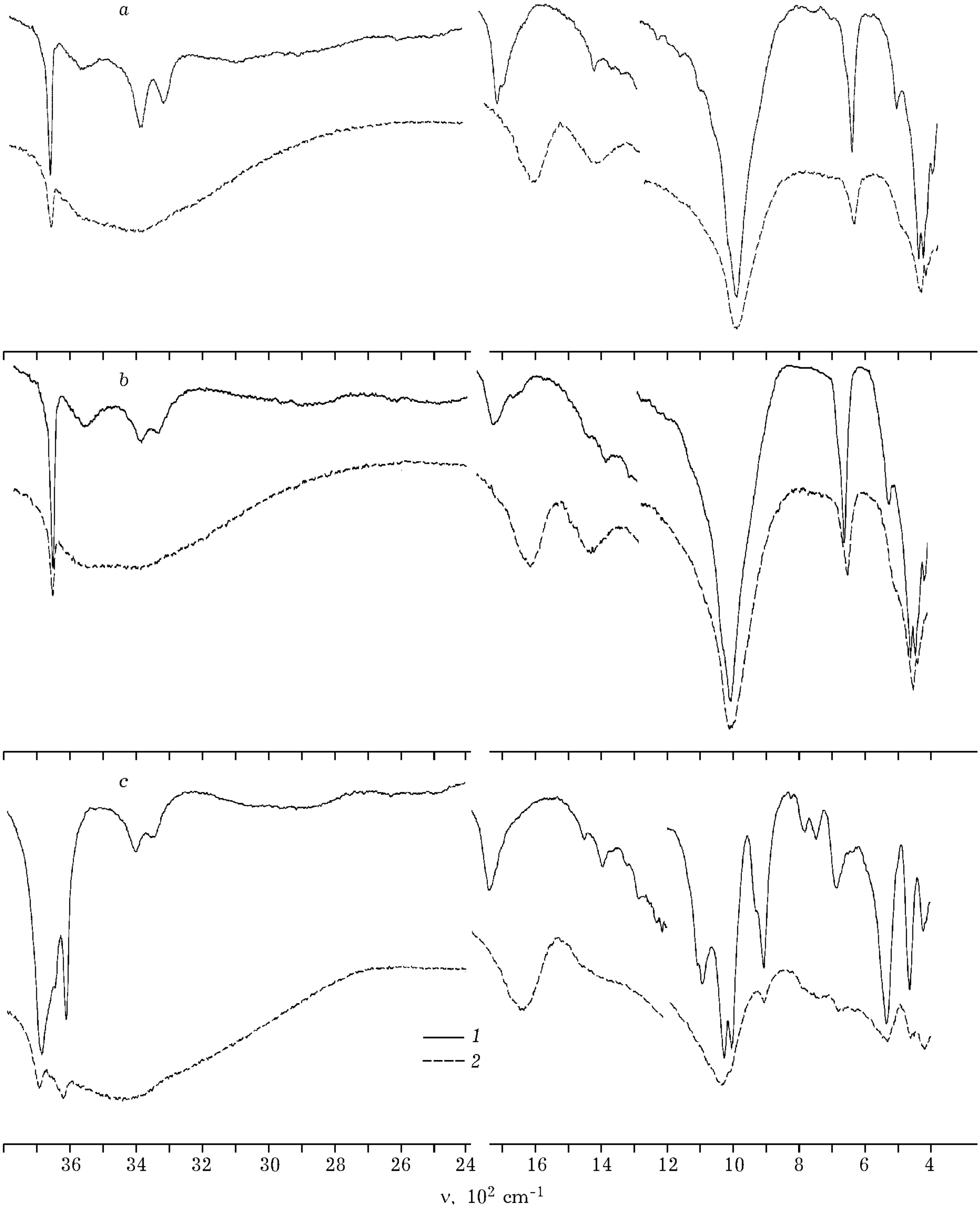

Fig. 4. IR absorption spectra of the mixtures: kaolinite – racemic acid (*a*), talc – racemic acid (*b*), talc – *l*(–)tartaric acid (*c*) before (*1*) and after activation for 1 min (*2*).

systems; because of this, below we present the analysis of the IR spectra for the MA of the mixture of kaolinite with racemic acid (Fig. 4, *a*).

Starting from activation time of 10 s, the IR spectrum of this mixture exhibits a decrease in the intensities of bands related to the vibrations of carboxylic groups (νOH, 3250–2450 cm^{-1}, ν_{as}C=O, 1735 cm^{-1}) and the appearance of the band which can be attributed to the vibrations of carboxylate ions ($\nu_{as}COO^-$, ~ 1650 cm^{-1} [7, 10]) and to the deformation vibrations of OH groups of water molecules formed during activation, which is confirmed by an increase in the intensity of absorption in the region 3550–2800 cm^{-1} [9]. At the same time, the intensities of the bands correspond-

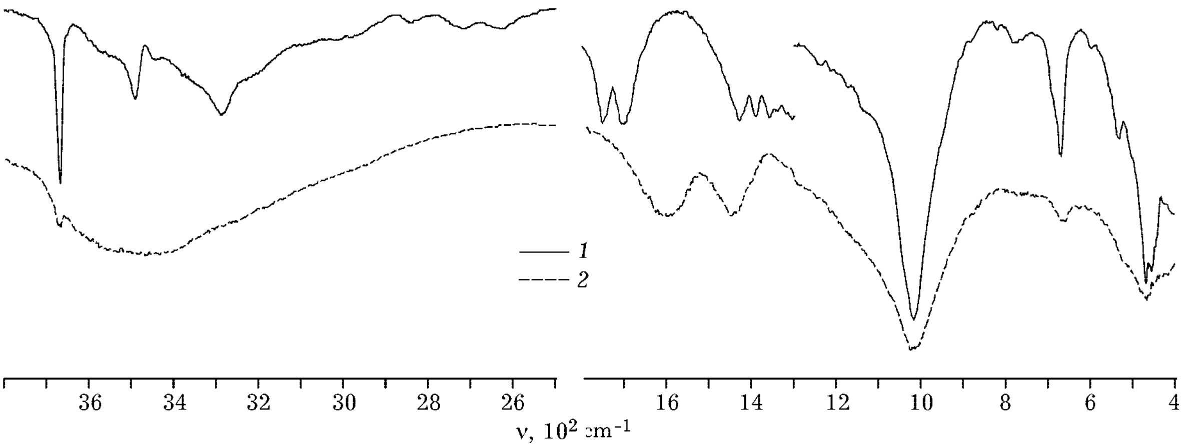

Fig. 5. IR absorption spectra of the mixtures of talc with citric acid before (*1*) and after activation for 1 min (*2*).

ing to the vibrations of kaolinite (νOH in the region 3800–3600 cm^{-1}; δOH – 940 см$^{-1}$; ν_{as}, ν_sSi–O–Si – 1115, 1110 и 685 см$^{-1}$) decrease [11, 12]. The intensity of the bands of stretching vibrations of hydroxyl groups of the acid at 3410 and 3350 cm^{-1} does not change at the initial stage of MA. After activation for 1 min (see Fig. 4, *a*) the bands of vibrations of the COOH groups of racemic acid disappear completely. Only the band of carboxylate ions remains, which is superimposed by the band of stretching vibrations of water molecules released during activation, with a maximum at ~1640 cm^{-1}. A broad band within the region 3550–2800 cm^{-1} corresponds to the stretching vibrations of water. The bands related to kaolinite undergo substantial changes, too: one broad band with the maximum at ~1040 cm^{-1} remains in the region of stretching vibrations of Si–O and Si–O–Si bonds, the intensity of the bands of stretching and bending vibrations of hydroxy groups decreases sharply. Changes in the IR spectrum of kaolinite mixture with racemic acid provide evidence that mechanochemical reaction of neutralization takes place during activation, similarly to the case of MA of kaolinite with fatty acids [1, 2, 13]. As a result, mechanocomposites are formed. The mechanochemical reaction starts almost from the very start of activation and proceeds for ~1 min. It is necessary to stress that in the IR spectra of the mixture kaolinite – racemic acid activated for 10 s the maximum of ν_{as}C=O band (1735 cm^{-1}) gets split into two maxima 1740 and 1730 cm^{-1}. This may be connected with the separation of the molecules of racemate into two optical isomers: *d*(+)-tartaric and *l*(–)-tartaric acids, or with the (partial) transformation of one optical isomer into another as a consequence of distortion of the lattice of the initial *dl*-acid during MA with kaolinite [4, 5, 14].

Changes in the IR spectra of the activated mixtures of kaolinite with citric acid are similar to the changes in the IR spectra of the mixtures of kaolinite with racemic acid described above. This allows assuming that the mechanochemical interaction in this system also starts almost with the very start of activation and occurs within 1 min.

Mechanochemical interaction in the system talc – hydroxy acid, independently of the number of carboxylic groups in the acid, proceeds with high intensity within 1 min and at the initial stage is participated by the carboxylic groups of the acid (see Fig. 4, *b* and 5). This is evidenced by a decrease in the intensity of vibration bands assigned to these groups till complete disappearance (νOH – 3250–2450 см$^{-1}$, νC=O – 1735 cm^{-1}) and the bands of hydroxo groups of talc molecules (νOH – 3675 cm^{-1}), appearance of vibration bands of carboxylate ions (ν_{as}COO$^-$ – 1650 cm^{-1}) and molecular water (δ – 1650 cm^{-1}, νOH – 3550–2800 cm^{-1}). We also observe a decrease in the intensity, some broadening and change in the shape of bands corresponding to the basic vibrations of talc (νSi–O$^-$ и Si–O–Si – 1020, 1040 and 670 cm^{-1}; δ_{layer} – 600–400 cm^{-1}).

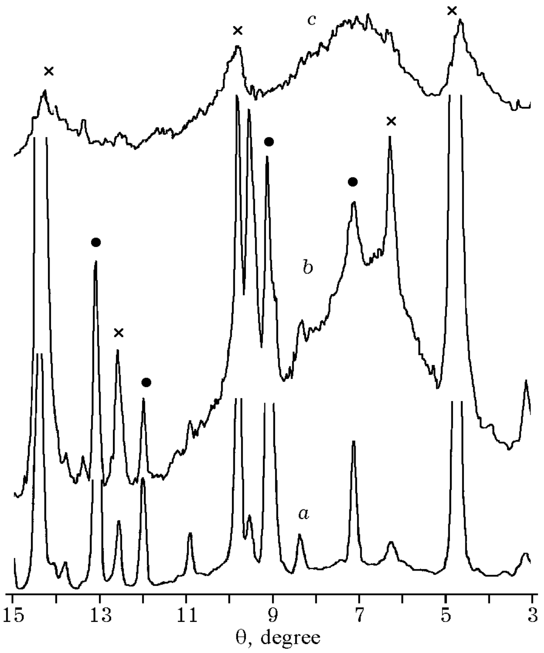

Fig. 6. X-ray diffraction patterns of the mixtures of talc with citric acid before (*a*) and after activation for 10 s (*b*) and 1 min (c): *1* – talc, 2 – citric acid.

In the diffraction patterns of mixtures of talc with hydroxo acids (for example, citric acid) activated for 1 min (Fig. 6), the diffractions related to the acid are absent, the intensity of reflections related to talc is decreased substantially, their broadening i observed, and a shift by no more than by 3 % with respect to the position in the initial talc.

The described data allow stating that the process of the joint activation of talc with hydroxo acids involves their mechanochemical interaction resulting in the formation of mechanocomposites, which inherit the lattice type of the initial talc.

It may also be assumed that the mechanochemical interaction between the silicate and a hydroxy acid proceeds only due to carboxylic groups. Hydroxo groups of the acids do not participate in the neutralization reaction. They are likely to form hydrogen bonds both with the hydroxo groups of the silicate and with water molecules formed during MA. This is confirmed by the investigation of solubility of mechanocomposites of hydroxy acids with silicates (the data are published in a separate paper). The absorption bands of hydroxy groups (3410, 3350 cm^{-1}) are observed for 20 s during activation of the mixtures with kaolinite and for 30 s during activation of the mixtures with talc. In course of further mechanical activation, they are masked by a broad absorption band in the region 3550–2800 cm^{-1} related to nOH of molecular water and hydroxyl groups held by hydrogen bonds [9, 11, 12].

CONCLUSION

Thus, new materials of the solid-phase cosmetics can be obtained mechanochemically. These include mechanocomposites based on natural silicates containing hydroxo acids and higher alcohols. In these mechanocomposites, the chemical bond between a silicate and an acid (alcohol) is determined by the nature of functional groups of the latter compounds. Mechanochemical interaction of silicates with solid-phase alcohols occurs due to the reaction of active groups of base character on the silicate surface with hydroxo groups. The reaction of silicates with hydroxo acid, independently of the number of carboxylic groups in the latter, proceeds *via* neutralization of the carboxylic groups of the acid with the surface groups of the silicate. Hydroxy groups of acid molecules are likely to participate in the interaction with silicates forming hydrogen bonds in the resulting silicates.

REFERENCES

1 T. F. Grigoryeva, I. A. Vorsina, A. P. Barinova, V. V. Boldyrev, *Neorgan. materialy*, 32 (1996) 214.
2 T. F. Grigoryeva, I. A. Vorsina, A. P. Barinova, N. Z. Lyakhov, *Ibid.*, 33 (1997) 998.
3 T. F. Grigoryeva, I. A. Vorsina, A. P. Barinova, N. Z. Lyakhov, *Ibid.*, 33 (1997) 993.
4 A. Ikekawa, S. Hayakawa, *Bull. Chem. Soc. Jpn.*, 61 (1988) 525.
5 A. Ikekawa, S. Hayakawa, *Ibid.*, 57, 5 (1984) 889.
6 Inventor's certificate 975068 USSR, 1982.
7 L. Bellami, The Infrared Spectra of Complex Molecules, Wiley, New York, 1961.
8 T. F. Grigoryeva, I. A. Vorsina, A. P. Barinova, N. Z. Lyakhov, *Neorgan. materialy*, 32 (1996) 84.
9 T. G. Balicheva, S. A. Lobaneva, Elektronnye i kolebatel'nye spektry neorganicheskikh i koordinatsionnykh soyedineniy, Izd-vo LGU, Leningrad, 1993.
10 G. Socrates, Infrared Characteristic Group Frequencies, New York, 1980.

11 A. N. Lazarev, Kolebatel'nye spektry I stroyeniye silikatov, Nauka, Leningrad, 1968.
12 I. I. Plyusnina, Infrakrasnye spektry mineralov, Izd-vo MGU, Moscow, 1977.
13 I. A. Vorsina, T. F. Grigoryeva, A. P. Barinova, N. Z. Lyakhov, *Khimiya v interesakh ustoichivogo razvitiya,* 8 (2000) 783.
14 Sadtler Research Laboratories Inc., Card No 148k, 16833k, 16834k.