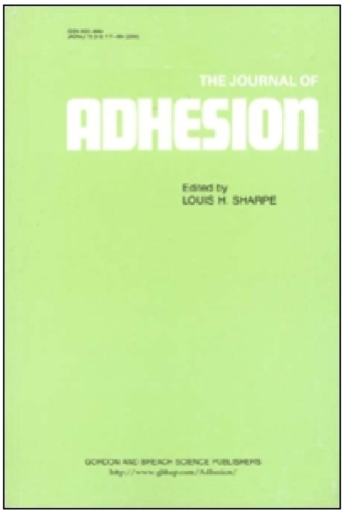

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Role of Autohesion During Film Formation from the Latex

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Role of Autohesion During Film Formation from the Latex

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I. THEORIES OF FILM FORMATION

As it is known not all dispersions of synthetic polymers can produce solid latex films upon drying.

Only dispersions with a polymer in high elastic or viscous flow state have such ability. Otherwise the film formation temperature should be either increased, or plasticizer or solvent should be introduced into the system.

It is difficult to judge the reasons leading to coalescence of particles. That is why up till now there has been no universal theory which can completely explain the process of film formation. Nevertheless, a number of theories were suggested, in which some attempts to explain this process were made. They include the theory of dry caking by Bradford.[1,2] According to this theory the film formation takes place under the action of surface tension. In the case of Brown's theory[3] the film is formed under the influence of capillary pressure, caused by surface tension at the water–air interface. The theory of wet caking, suggested by Vanderhoff and Bradford,[4] invokes the action of surface tension at the polymer–water interphase. Sheets,[5] as well as Brown, thinks that the start of film formation is caused by capillary forces, but subsequently after quite strong film packing water diffusion through the film begins to play a dominating role.

Voyutskii and Shtarkh[6] have suggested the so-called autohesive theory, according to which the autohesion phenomena are the main ones in the last stage. Autohesive theory does not deny the role of another cause at the beginning of film formation but the last stage of solid and strong film formation as a result of autohesion seems to be the most important.

II. MODERN NOTIONS ABOUT AUTOHESION

According to diffusion theory,[7] autohesion is a particular case of adhesion and is caused by self-diffusion. Polymer interpenetration takes place as a result of thermal movement of macromolecule segments, due to this fact a strong bond occurs between the polymers. For interpenetration, of course, the polymers (or at least one of them) must be in a viscous or high elastic state. In addition they have to be partly compatible. In this case the polymers can possess no thermodynamic compatibility as a result of the adhesion arising at the expense of the so-called "local diffusion" or "segmental" diffusion.[8,9]

It is essential that adhesion or autohesion are attributed to the main peculiarities of polymers, namely to chain structure and molecular flexibility permitting them to change their conformations on account of thermal movement.

According to the diffusion theory the autohesive or adhesive bond formation is caused mainly by entropy increase as a result of surface molecules interentanglement on both polymer layers, brought into contact, the ends of these molecules being in thermal movement.

It is quite obvious that as a result of diffusion the interface between polymers is washed out and disappears and a peculiar intermediate layer is formed, representing the gradual transition from one polymer to another. Therefore adhesion of polymers is essentially not a surface but a volume phenomenon and adhesive strength is caused not by the forces at the initial contact interface, but by the strength of the formed transition layer. The forces providing the strength of the transition layer are, of course, the usual intermolecular forces.

Besides the common considerations pointing to the great importance of diffusion phenomena in autohesive and adhesive bond formation between polymers, there are a lot of experimental facts confirming the justice of this point of view.

Until the present time only indirect evidence, and mainly the dependence of bond strength between two polymer layers upon time and temperature, served as a corroboration to the validity of diffusion theory for adhesion and autohesion of polymers. In this case such kind of explanation as the bond strength rise with contact area increase is not justifiable, because autohesion or adhesion increase with time or temperature has been observed in the case when such pressures are used which provide full contact of the surfaces,[9] or when one of the polymers is applied in a solution form on the layer of another polymer, i.e., when full contact of adhesive and substrate is doubtless.

The diffusion theory is well confirmed by the adhesion or autohesion dependence upon the value, shape, crystallinity, polarity and orientation of polymer molecules. All this has been stated in the known monograph by Voyutskii.[7] The effect of factors which increase polymer diffusibility is always in correlation with the influence of these factors on adhesion or autohesion.

Until the present time we had few direct evidences of polymer interpenetration when forming autohesive or adhesive bonds, although we had more than enough indirect evidences of the validity of the autohesion diffusion theory. The reason is in the experimental difficulties arising when such a problem is being solved.

The methods used for the direct determination of the role of diffusion when forming autohesive or adhesive bond include radio labelled atoms, usual microscopic observations, ultra-violet induced luminescence and electron microscopy.

Bueche with co-workers[10] for the first time and somewhat later Bresler with co-workers[11] have carried out the measurement of polymer self-diffusion using a labelled atoms method. According to this method a thin coat of radioactive substance is applied on a flat block prepared from the substance of the same origin but without any radioactivity. As the radioactive polymer diffuses into the non-radioactive one, the radiation intensity of β-particles measured by a counter placed above the sample is decreased due to the radiation absorption by the substance of the block. Thus the diffusion speed may be judged by the decrease in radiation intensity.

The presence of macromolecular diffusion in the case of contact of compatible polymers has been shown in both works, the diffusion coefficient being in the order of 10^{-11}–10^{-14} cm^2/sec. If one of the polymers is a vulcanizate then the diffusion coefficient is sharply decreased, just as is expected.

Krotova and Morozova[12, 13] have studied interdiffusion by observing, under the optical microscope, sections of two-layer films, prepared from different polymers. It was found that when two non-polar or weak polar polymers are in contact the interphase is washed out. Based on this fact it was concluded that in this case adhesive bond formation is caused by the interdiffusion process.

By means of microscopic observations in ultraviolet rays the same authors have studied the interphase between polymers with luminescent properties. The observations have shown that the interphase is always strongly washed away when the systems consist of non-polar elastomers with other molecules of similar structure. In this case the thickness of a transition layer may be 10 μm. Unfortunately, the light microscopy methods which permit clear determination of the interphase washing out due to interdiffusion of some polymers with highly flexible molecules, or polymers with low molecular weight, cannot give data about processes in the contact zone of polar polymers strongly different in polarity. In the last two cases the thickness of the transition layer, formed due to polymer diffusion, may be so small that it cannot be detected by normal microscopy. The answer to this question was obtained by means of the electron microscope, as its resolution is two orders higher than that of the light microscope.

Voyutskii with co-workers[14] has carried out the electron microscopic study of transverse, superthin sections from two-layer samples, the last being prepared at different temperatures and pressures using various pairs of polymer films.

Microphotometry of the obtained pictures in the direction perpendicular to the contact margin was used for more exact determination of the washed-out, zone, i.e., the depth of one polymer permeation into another. The photometry of the pictures has shown that the steady change of optical density in the contact zone at one polymer transition into another may be explained only by diffusion. In this case the interface washing out was the higher, the better was the polymers compatibility, the higher was the layering temperature and the longer the samples were subjected to high temperature.

Zlatkevich with co-workers[15] has found by means of a radiothermoluminescence method the presence of a transition layer in partly or fully compatible elastomers as well as the validity of diffusion theories during transition layer formation.

Aivozov[16] also has concluded that there is an interphase transition layer between two polymers of poor mutual solubility. These data were obtained by using the method of mechanical loss determination when measuring dielectric permeability, as well as by nuclear magnetic resonance.

Recently,[17] the so-called method of paramagnetic probe was used to prove the interdiffusion of two thermodynamically incompatible polymers. This method is based on the rotating mobility investigation of stable radicals in a polymer matrix. The application of stable radicals as a paramagnetic label once more has confirmed the possibility of diffusion of macromolecule ends at the contact margin of two thermodynamically incompatible polymers.

Naturally, the above given evidences of transition layer formation between two polymers of different nature are attributed also to autohesion, because it is only a particular case of adhesion.

Theoretical interpretation of the phenomenon may serve as corroboration to the validity of polymer diffusion theory, if it is confirmed by the experimental results. Proceeding from the premises suggested by Vasenin[18] and still earlier by Voyutskii[7] and considering particularly that the molecules of one polymer diffuse into another mainly by their ends, Voyutskii and Vasenin with co-workers[19] have quantitatively interpreted the data obtained when studying the effect of the molecular weight of polymers on kinetics of autohesive bond formation.

III. ROLE OF AUTOHESION DURING FORMATION OF LATEX FILMS AND POLYMER DISPERSIONS

A series of phenomena and processes occurring in polymer processing technology, particularly film formation both from latex and polymer dispersions can be explained by self- and interdiffusion.

The process of film formation from rubber latex under normal conditions proceeds rather slowly and passes through a series of successive stages,[6] followed by dewatering.

The last stage seems to be the most important, because it is here that the film acquires a characteristic structure and desirable mechanical properties. At this stage, as a result of gradual water loss, the stabilizer molecules in one case are gathered into separate aggregates of globules and the stabilizer may remain in the film as a dimensional network; in other cases the emulsifier is dissolved in the polymer and in this way it gradually disappears from the surface of the globules, in this case softening the polymer and speeding up the film formation.

The places uncovered by a stabilizer are formed as a result of the stabilizer disappearance from the surfaces of the globules, at the expense of these places the rubber–rubber contact takes place and such a polymer property as autohesion begins to play a considerable role. It is just the autohesion which determines the course and degree of interaction of the rubber globules and thus a number of the final film properties. Strong sticking of the globules may be accomplished only in the case when the polymer has a sufficient degree of autohesion. The higher the autohesion, the quicker is the sticking and coalescence of the rubber globules, when other conditions are equal. In particular, the autohesion explains the effect of rubber plasticity on the properties of the resulting latex film,[6, 20] improvement in film formation with temperature increase[6, 21] and plasticizer introduction.[6, 22]

Otherwise speaking, physical contact of two polymer particles and interface elimination between them are not sufficient for the strong bond formation between the particles. For a strong film production the parts of the polymer molecular chains have to diffuse from one globule into another, forming a strong bond between them. In other words, in order to produce a strong and elastic film a strong transition layer has to be formed between the globules, the structure of the layer being close to that of any other place in the globule of the film forming polymer.

In the case when the autohesion of the film forming substance is good, when emulsifier quantity is low and it can be dissolved in the polymer, then the coalescence of globules may go so far that the film in the end will represent a homogenous system, i.e., a true solution of emulsifier in the polymer. Such a film has properties similar to those of the pure polymer.

The film will be microheterogeneous, when emulsifier content is high and its solubility is poor. In this case, the residues of the undissolved emulsifier will be the continuous phase of the film, and the polymer will be the dispersed phase. Such film structure resembles an emulsion of the second order. By analogy with emulsions, we call such films, films with a structure close to second order.

It should be noted that such microheterogeneity may not only worsen the film properties but increase its strength. For example such a phenomenon is observed in natural latex films. Apparently native albumen in this case acts as an active filler for latex polymer.

When emulsifier solubility in the polymer is still lower and its content is higher, then a film is formed representing two interpermeable networks from an emulsifier and a polymer; that is, a film with "open" structure. Apparently in this case there will be through capillaries in the film, filled by the hydrophillic emulsifier. By means of these capillaries polar liquid (water, for example) may permeate into the depth of the film, leading to its considerable swelling. Presence of the same capillaries provides the possibility for emulsifiers and other water soluble substances washing away.

At last with large amount of the emulsifier with low degree of solubility in the polymer, a film is formed representing the polymer particles surrounded from all sides by the emulsifier. By analogy with emulsions we call such films the films with a structure close to first order. These films, however, are usually of no practical importance, because they are easily redispersed in water.

The ideas developed by Voyutskii and concerning film forming processes from the autohesion point of view have found circulation among the foreign scientists as well.

Thus Bradford and Vanderhoff,[23] studying by electron microscopy the morphological changes in the films from styrene-butadiene latex, and the effect of additives during film productions, have concluded that their experimental data are accounted for the autohesion theory. Brown[24] has noted, that not only surface tension at the water-air interface and capillary forces, but autohesion processes as well are the moving forces in the film forming process.

IV. THE FILMFORMING PROCESS IN THE CASE OF VULCANIZED LATEX

Autohesion and film formation are also possible when latex globules have been vulcanized (vultex, revultex).

Mechanism of solid film formation from vulcanized latex is of great theoretical and practical interest. However, the literature concerning both the problems of the latex vulcanization and film formation from vulcanized latex is rather limited.

The film formation process and its mechanism are greatly influenced by the autohesion of the high polymer, by the nature of the stabilizer contained in the dispersion and by the rubber vulcanization of latex globules. In order to find out the influence of the bond origin, arising in the film between separate globules and "network" of the protective substance, on the film forming mechanism we have determined the physical–mechanical properties of the films before and after vulcanization; the films were subjected to swelling in water vapours and in hydrocarbon, to rupture at elevated temperature and to mechanical processing.[25, 26] In addition, the latex and films prepared from them before and after vulcanization were studied by means of electron microscopy.

We studied the films prepared from the unvulcanized natural and styrene–butadiene latex SKS–30, containing 30% of styrene residues. As is known, the degree of coating of the surface of the latex globules by a stabilizer is higher when natural latex is used in comparison with synthetic latex SKS–30.

The difference in the behaviour of the rubber films, prepared from natural and synthetic latex, caused by different nature, quantity and localization of protective substances was distinctly seen when effects of vulcanization conditions on the properties of the latex films were compared.

Vulcanization condition (in latex and in the film, vulcanized in a dry form) exerts influence over the strength of the film when natural latex is used and has practically no effect when the synthetic latex is used.

Swelling in water vapour strongly decreases tensile strength of the films produced from the vulcanized natural latex. The strong decrease of tensile strength in a vulcanized natural latex film upon swelling in water vapour is attributed to the swelling and decrease in strength of the native albumen contained in the film. Besides, the swelling of albumen in the spaces between globules, probably leads to the globules moving aside from each other. The latter, of course, also has to weaken the strength of the system.

In the case of synthetic latex SKS–30 the strength of the films produced from the vulcanized latex and that of the films vulcanized in a dry state, practically is not changed upon swelling in water vapour.

Effect of swelling of films in vaseline oil on the strength of the films prepared from the natural and synthetic latex SKS–30 leads to the decrease in tensile strength with swelling in the films of the unvulcanized natural latex.

Decrease in tensile strength at high degrees of swelling leads to the sharp weakening of the films prepared from the vulcanized natural latex. Such sharp weakening of strength at swelling was not observed in the films vulcanized in a dry state. A characteristic feature of styrene–butadiene latex is an approximately equal decrease in strength at swelling in vaseline oil both for the vulcanized latex films and for the films vulcanized in a dry state.

Effect of the test temperature increase on tensile strength of the natural and styrene–butadiene latex films results in strength decrease in all films. An especially sharp strength decrease (by 80 and 88%) was observed in the unvulcanized and vulcanized natural latex films. The films vulcanized in a dry state lost only 33% of their strength at the same temperatures.

With test temperature increase the strength decrease is approximately equal in the vulcanized latex SKS–30 films and in the films of the same latex, vulcanized in a dry state.

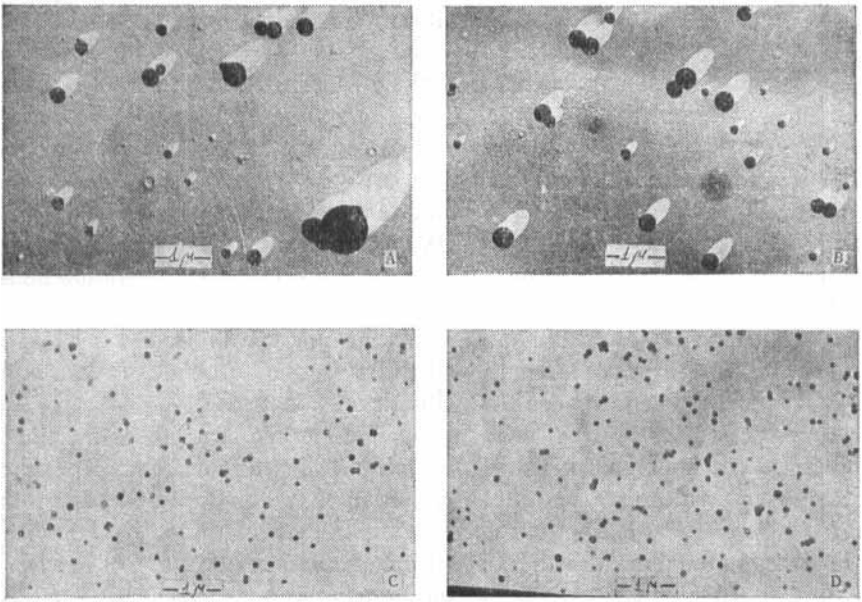

FIGURE 1 Electron micrographs of latex before and after vulcanization: a—original natural latex; b—the same, vulcanized; c—original SKS–30 latex; d—the same, vulcanized.

Upon milling the films the distinctions between vulcanized and unvulcanized synthetic latex films were clearly seen, but natural latex was practically free of them. On milling, the film from unvulcanized and vulcanized natural latex gave the "skin" which is usual for a rubber, while the vulcanized styrene–butadiene latex film on milling turned to crumb.

Thus these experiments have shown, that during film formation from unvulcanized and vulcanized natural latex the separate globules are connected to a great extent by intermolecular forces. When latex SKS–30 based film is formed its protective substance seems to be insufficient to form a solid network and the film has a great number of direct rubber–rubber contacts. Naturally this is what promotes interglobule chemical bond formation after not only dry film vulcanization, but at vulcanization in latex as well.

Electron microscopy has shown,[27] that size of latex particles and their shape is maintained after both natural and synthetic latex vulcanization. It is clearly seen from Figure 1, where electron micrographs of these latex particles are shown before and after vulcanization.

Proceeding from the above, it may be considered that vulcanization must not influence to a high extent the packing of globules during the film formation from vulcanized latex.

The electron microscopy investigation of the film structure, given in Figure 2, has shown that during the natural latex film formation (Figure 2a) the globules are easily and comparatively loosely packed and their external coats when they are in contact form a network penetrating the total depth of the film.

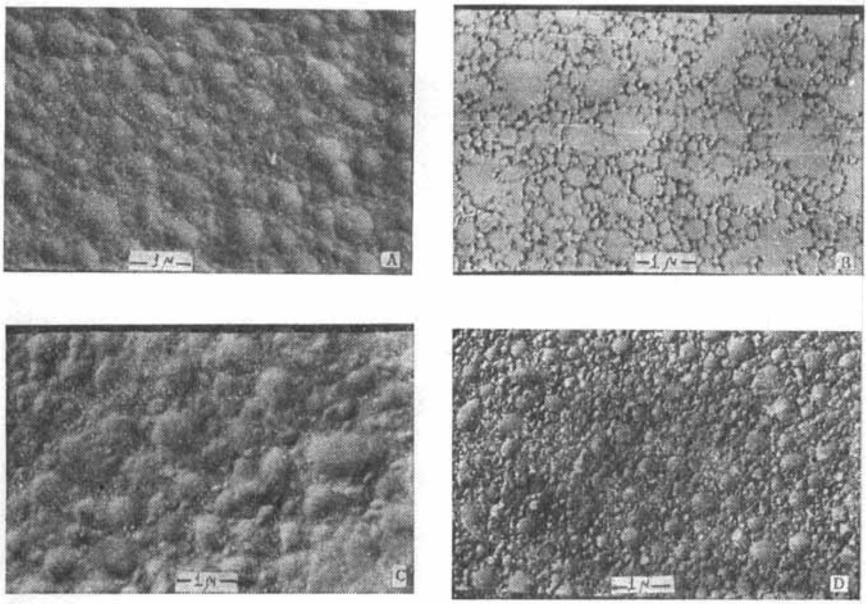

FIGURE 2 Electron micrographs of replica from the film surface of unvulcanized and vulcanized natural latex before and after thermal processing: a—a film of the original natural latex; b—the same after thermal processing; c—the same after 8 months storage; d—the same from vulcanized natural latex.

During film formation the protective coats in some places are broken and the contact of the inner rubber content of the adjacent globules takes place. From the moment of the polymer–polymer contact autohesion of the polymers begins to be of vital importance in elastic film formation; it increases with temperature rise (Figure 2b) and with period of contact (Figure 2c). That is why the thermal processing of original natural latex films leads to a large coalescence of rubber globules. In vulcanized latex films (Figure 2d) the sticking of globules is poorer, caused both by albumen denaturation and the crosslinking of polymer molecules in the globules, promoting the decrease of the autohesive processes.

When the unvulcanized natural latex films were stored during a long period of time the gradual washing out of the outlines of the latex globules was observed, testifying to the continuation of polymer diffusion, leading to the better coalescence of globules. The sticking of the globules was not complete and this may be attributed both to the slow processes of autohesion and to the presence of residues of the stabilizer fractions (of native albumen) on the surface of globules, which are badly dissolved in the polymer.

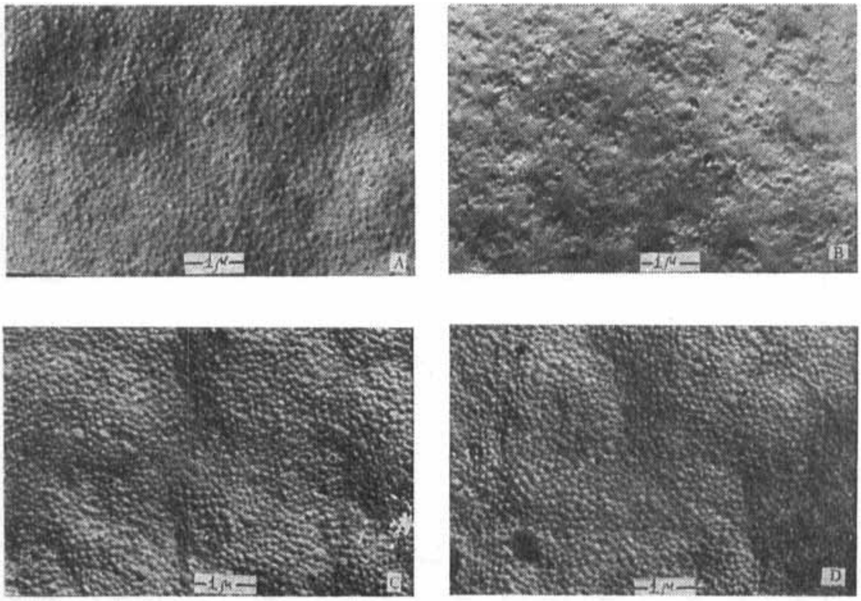

FIGURE 3 Electron micrographs of replica from the film surface of unvulcanized and vulcanized SKS–30 latex before and after thermal processing: a—a film from original latex; b—the same after thermal processing; c—the same from vulcanized latex; d—the same after thermal processing.

The nature of the emulsifier in the original latex is an important factor, determining this or that film structure; it is confirmed by the electron microscopy pictures of replicas from the SKS–30 latex films, shown in Figure 3. One can see the separate globules on the replica taken from the surface of the film, produced from the starting styrene–butadiene latex (Figure 3a), whose protective coatings consists of the fatty acid salts and does not cover the whole surface of the latex particles. These separate globules are not in such isolation as in the case of natural latex. Thermal processing of the same films (Figure 3b) promotes the considerable coalescence of globules, which is apparently caused by a great number of rubber–rubber contacts as well as by better emulsifier solution in a polymer in comparison with native albumen. The films of the same latex, but preliminarily vulcanized (Figure 3c) also have the globular structure, but the margins of the separate globules are represented less distinctly, than in the films produced of vulcanized natural latex. In this case thermal processing weakly promotes the globules' coalescence (Figure 3d).

CONCLUSION

The above given data have evidently shown that the reason for the different structures in the film forming process should be searched for not only in the polymer nature, but in the nature and amount of the protective substances present in the latex.

It seems to us that all above described properties of the vulcanized latex films may be easily explained on the basis of diffusion concepts, given above. Indeed, when the state of vulcanization is not too high the free ends or loops of macromolecules are left on the surface of the latex globules. During the film forming process these macromolecular ends and loops are able to interdiffuse and as a result to form a sufficiently strong bond between the adjacent globules. Swelling of the emulsifier residues in polar liquids promotes the moving apart of globules thus helping "to pull out" the ends of the macromolecules and weakening the bond strength between the globules. Polymer swelling in hydrocarbon medium as well as temperature rise also leads to the bond strength weakening between the adjacent globules thus promoting the strength decrease in the vulcanized latex films. All this confirms the basically physical character of the bonds between the vulcanized globules even if in natural latex.

When the films were vulcanized in a dry state then chemical bonds arise between the molecules of the adjacent globules and the tested factors affect these bonds to far less degree.

The validity of the given explanations is especially clearly confirmed by the fact that the films of vulcanized natural latex can produce "skin" on milling, while the films vulcanized in a dry state do not possess such ability.

All these regularities are far less clearly expressed in synthetic latex SKS–30. This points to the fact, that in the case of SKS–30 latex the chemical bonds arising are of far greater importance. As has already been stated, the latter may be attributed to the smaller thickness of the emulsifier protective layer in SKS-30 latex, which promotes the formation of chemical bonds between the molecules of the adjacent globules still in the latex or at the beginning of the film formation.

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