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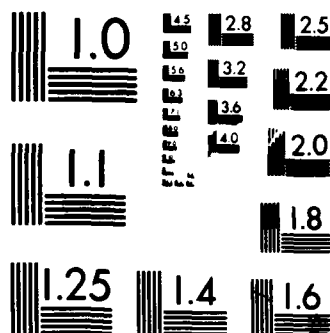
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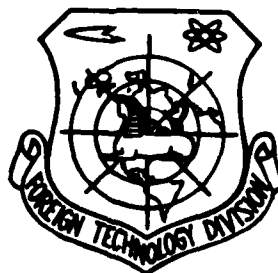
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HIGH-MOLECULAR COMPOUNDS
(Selected Articles)



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FTD-ID(RS)T-0397-87

22 June 1987

MICROFICHE NR: FTD-87-C-000435

HIGH-MOLECULAR COMPOUNDS (Selected Articles)

English pages: 19

Source: Vysokomolekulyarnyye Soyedineniya, Seriya B,
Kratkiye Soobshcheniya, Vol. 9, Nr. 7, September
1967, pp. 491-492; 493-494; 494-495; 511-514

Country of origin: USSR

Translated by: FLS, INC.

F33657-85-D-2079

Requester: FTD/TQTR

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Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

Page 51.

However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

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U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ѣ in Russian, transliterate as yě or ě.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh ⁻¹
cos	cos	ch	cosh	arc ch	cosh ⁻¹
tg	tan	th	tanh	arc th	tanh ⁻¹
ctg	cot	cth	coth	arc cth	coth ⁻¹
sec	sec	sch	sech	arc sch	sech ⁻¹
cosec	csc	csch	csch	arc csch	csch ⁻¹

Russian	English
rot	curl
lg	log

GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc.
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UDC 678.744:678.01:53

CRYSTAL BANDS IN THE INFRARED SPECTRUM OF POLYMETHYLMETHACRYLATE IN THE AREA OF 1,500-1,700 cm^{-1}

P. Sedlachek, S. Sykora, B. Shneyder

Submitted 30 January 1967

Bands have been observed [~~1,2~~] in the area of 1,500-1,700 cm^{-1} in the IR-spectrum of polymethylmethacrylate [PMMA]. The intensity and form of these bands is attributed to the crystallinity of the samples. We checked the measurements on a large series of PMMA samples, the behavior and block form of which, as determined by the nuclear magnetic resonance [NMR] [~~3~~] spectra, are significantly different from one another. We took the IR-spectrum for each sample of a film which was obtained from a 2% solution of CHCl_3 , a spectrum from the same film after swelling it for 16 hours in 4-heptanone [dipropyl ketone], and, finally, a spectrum of the same film after thermostatic control at 120° for two hours (Figure 1). [Note: See pages 3 and 4 for Figures.] After such processing, we observed the sharp bands in the IR-spectrum, reported in works [~~1,2~~], only in those samples whose initial spectrum contained a broad weak band in the area of 1,550-1,650 cm^{-1} . The intensity of these bands was not connected

→ (Russian translation) 1

with the sample's stereospecific structure. Intensive bands in the area of $1,560-1,580\text{ cm}^{-1}$ of the IR-spectra weaken and become broader when a film obtained through forming it on a KBr disk is acted upon by methanol (Figure 1c). After removing the film from the disk, it was established that the film's spectrum generally does not retain such a band (Figure 1d). There is a band at 1580 cm^{-1} in the IR-spectrum of the disk itself (Figure 1e). The intensity of this band is comparable to the intensity of the CO band in the remaining PMMA. Therefore, we extracted powdered PMMA with methanol and established that during secondary extraction the intensity of the band in the area studied decreased smoothly (Figure 2). In the IR-spectrum of the dry residue of the methanol extract there are, in addition to the weak bands of PMMA, stable lines which pertain to sodium acetate (Figure 3a, 3b). It is interesting that the action of the 4-heptanone on the dry residue causes splitting in the band at 1580 cm^{-1} into a doublet similar to the one that was found in the polymer (Figure 3c). We therefore established that the action of 4-heptanone on the sodium acetate causes a change in the latter's spectrum. On the basis of the results we obtained, we think that the presence of the bands in the area we looked at are caused not by PMMA, but by the unintended presence of acetate.

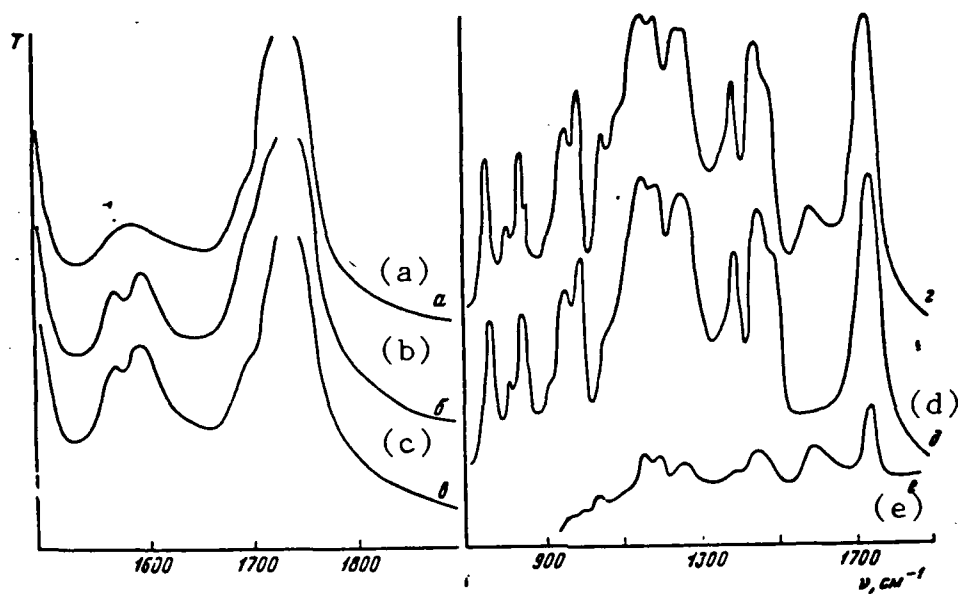


Figure 1 IR-Spectra of film prepared from a 2% solution of isotactic solution of PMMA in CHCl_3 deposited on a KBr disk with the following processing.
 a - source; b - swelled over 16 hours in 4-heptanone; c - held for two hours thermostatically at 120° ; d - removed from the KBr disk; e - IR-spectrum of the KBr after the film was removed.

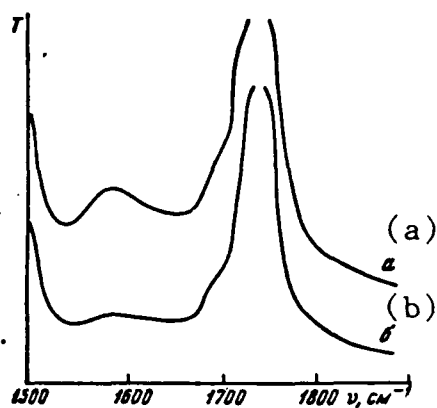


Figure 2. IR-spectra
a - disk made from the initial PMMA sample (see Fig. 1a); b - disk made from that PMMA sample twice extracted with methanol for 12 hours

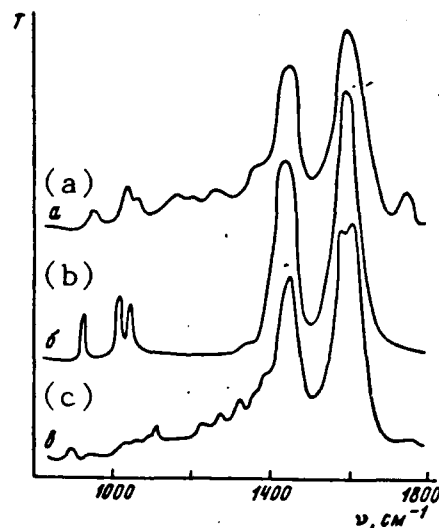


Figure 3. IR Spectra:
a - extract after washing the film (Fig. 1d) with methanol evaporated on a backing of NaCl; b - sodium acetate in the KBr disk; c - extract (see 3a) which was held for 16 hours in 4-heptanone

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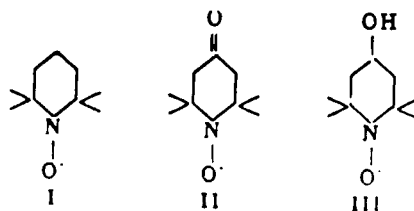
MIGRATION OF STABLE RADICALS IN POLYMERS

V.B. Stryukov, Yu.S. Karimov, E.G. Rozantsev

Submitted 30 January 1967

Dear Editor:

As is known, the compatibility of antioxidants with polymers has significant value in the problem of stabilizing polymer materials. We observe that a series of inhibitors with free-radical character, for example 2,2,6,6-tetramethylpiperidine-1-oxyl (I), 2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl (II), and 2,2,6,6-tetramethyl-4-oxypiperidine-1-oxyl (III) easily diffuse in various polymers upon contact with the latter.



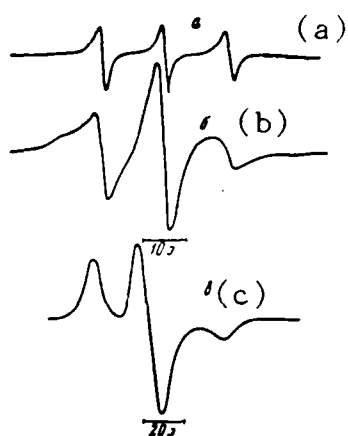


Figure 1. EPR signal of radical I in various polymers: a - polydioxalane, 293° C.; b - polyvinyl chloride, 293° C.; c - polyethylene, 77° K.

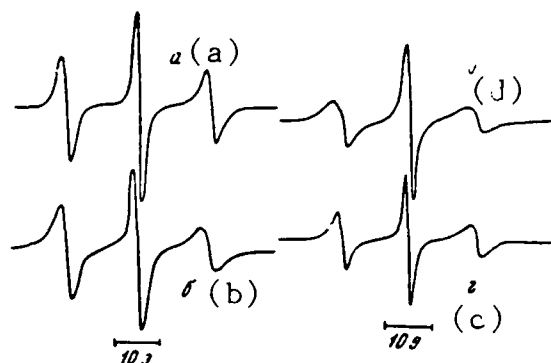


Figure 2 EPR signal of various radicals in polyethylene at 293° C. a - radical I; b - radical III; c - radical II in a deformed sample; d - radical II

When the polymer sample is held in air and dried with iminoxile vapors, the latter will diffuse into the interior of the polymer after several minutes. As the basic method for studying the migration of radicals into the polymer material, we used the method of electron paramagnetic resonance [EPR]¹. At room temperature the spectra of the EPR radicals which had penetrated into the interior of the polymer look like a well-resolved triplet, characteristic of a diluted viscous

¹. Measurement were conducted using a RE-1301 spectrometer, $\nu = 9,300$ MHz

solution of stable iminoxiles [1], but the polymer's nature exerts significant influence on the features of the EPR spectra (Fig. 1).

Since the sequencing of the width of the line of super-thick structure (STS) is connected with molecular rotations [2,3], the difference in the EPR spectra must be taken due to the varying rate of rotational movement of the iminoxiles in the corresponding polymers. Doubtlessly the symmetry, the volume, and the stereochemical configuration of the radical also will influence its rotational movement in the polymer (Fig. 2).

With a change in sample temperature, the shape of the spectrum changes; thus with a decrease in temperature each STS component gradually widens by the law of variation, and near the temperature of liquid nitrogen (77° K.) the EPR spectrum takes on an asymmetrical character (Fig. 1c).

It is significant that during deformation of poured samples of polyethylene, the STS picture of the EPR spectrum for the included radical significantly changes (Fig. 2c), which leads to a decrease in the movement of the radicals in the deformed polymer.

Based on these experiments, which we conducted on many varying polymer materials, we can conclude that the EPR method is useful not only to study migration of the most stable radicals in a polymer, but also for studying the diffusion and behavior of stabilizer molecules which leave a paramagnetic signature.

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UDC 66.095.265:678.744

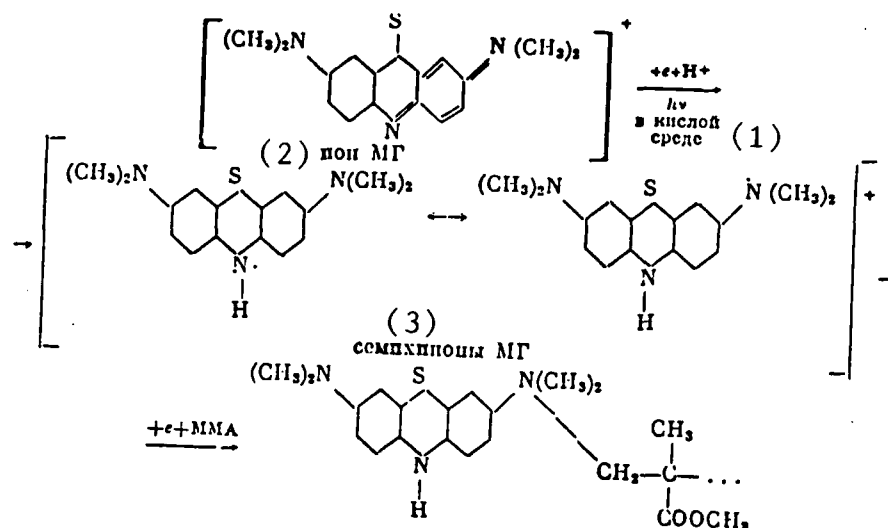
DYE ENTRANCE INTO THE POLYMER CHAIN DURING SENSITIZED PHOTOPOLYMERIZATION
OF METHYLMETHACRYLATE THROUGH THE PHOTOREDUCTION MECHANISM

V.V. Gavrilov, V.I. Kosyakov

Submitted 13 November 1967

Dear Editor:

We studied photopolymerization of methylmethacrylate [MMA] sensitized to long-wave visible light. As a sensitizer we used the dye methylene blue [MB], reduced through the action of red light in the presence of triethanolamine (TEA) [1]. Proposing the radical mechanism for sensitized photopolymerization in the system studied, we believe that the role of initiator is played by the semiquinone MB, which is formed at the intermediate stage of the transformation of the dye into a leuco-compound during light absorption. With this mechanism the initiation of the dye molecules in the form of a leuco-compound will enter the polymer chain as end groups:



Key: (1) In an acid medium; (2) MB ion; (3) semiquinone MB

Actually, in the absorption spectrum for the polymer film we managed to observe a clear maximum at $\lambda = 256$ nm, which corresponds to the maximum state as presented in work [2], and also is observable for the "free" leuco-compound MB in the solution. This fact, in our view, convincingly confirms the proposed mechanism for MMA photopolymerization, when the MMA is sensitized to long-wave visual light by MB dye.

The parameters of the reaction system: Photopolymerization of MMA was conducted on a mass at 30°, using exposure for 40 minutes at an illumination intensity of 100 mW/cm² in a fixed area of the spectrum from 580-720 nm. Component concentration: MB = $1 \cdot 10^{-3}$ mole/l; TEA = $2 \cdot 10^{-1}$ mole/l; [HCOOH] (Regulator of the eH medium) = $8 \cdot 10^{-3}$ mole/l. Purity of the products: MMA $n_D^{20} = 1.4132$; boiling point 100°, TEA $n_D^{20} = 1.4852$.

During preparation of the film, the photopolymer was separated from non-reacted MB and TEA through five-fold reprecipitation until complete disappearance of any absorption in the visible area of the spectrum.

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UDC 678.744:678.01:53

THE ROLE OF ELECTRIC PHENOMENA IN FRICTION OF POLYMETHYLMETHACRYLATE

A.I. Yelkin, V.N. Nikolayev

Moscow Pedagogical Institute imeni V.I. Lenin

Submitted 26 May 1966

In studying friction of polymethylmethacrylate we observed that in the atmosphere there is observed a growth in the friction force with an increase of the number of test cycles up to a determined value, while at the same time in a vacuum we measured essentially no change in the force of friction as the number of test cycles increased. During each test cycle the sample of polymethylmethacrylate, under load, was slid along a polished steel surface at a constant rate (v) for some distance (S), and then with the same speed it was returned to the starting position. Differences in the friction surface were excluded in this way.

This work has the aim of clarifying the relationship of an increase

in friction force in the process of sliding in atmosphere due to the appearance of charging of the polymer.

The influence of charging on external friction is known from the works of Deryagin and Smigli [1], Dubinin [2,3], and other authors [4-6]. However this matter is still lightly studied.

In this work we compared the relationship of friction force and the potential of the electric field with the number of test cycles when sliding polymethylmethacrylate along a metal surface in a vacuum and in the atmosphere.

The research was conducted on a vacuum tribometer [7]. The potential of the electric field, which was proportional to the charges which arose on the friction surface pares, was measured on the instrument which Rayevskiy [8] developed.

Figure 1 presents the curve of the friction force (F) in relation to the number of test cycles (n) under atmospheric conditions. During the first test cycle the friction force had the value F_0 . During each new cycle the friction increases. However, the force of friction after a determined number of tests reaches saturation and further tests do not increase the value of F_{∞} . If the friction surfaces are separated and discharged, then the friction force for subsequent tests begins to increase again from value F_0 to F_{∞} (Curve 2, Fig. 1).

An analogous form is found in the relationship of the potential of the electric field near the surface of the polymer sample in standard units compared to the number of test cycles (Fig. 2, Curve 1). Saturation of the force of friction and the electric potential become approximate after the same number of tests (8-12).

Electrostatic charging of the dielectric in the course of any action on them has a limited intensity [9] under given external conditions. In the course of friction of the polymer on the steel surface (Fig. 2, Curve 1) there takes place an uninterrupted charging of the polymer samples up to a determined intensity, depending on the nature of the interacting surfaces, temperature, and so on.

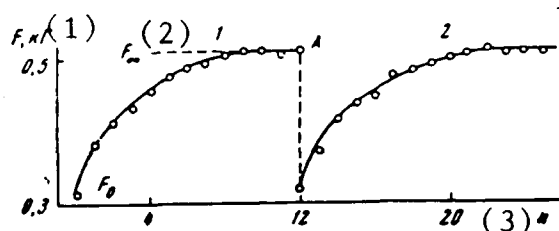


Figure 1. The relationship of the force of friction (F) of polymethylmethacrylate on steel upon the number of test cycles (n). Point A corresponds to the moment of separation of the surfaces of the friction pair, their discharge, and putting them again into contact; the rate of sliding is 125 mm/min; the standard load is 2 kg; the area of nominal contact is 2.3 cm²; 1 and 2 are test cycles.

Key: (1) F , kg; (2) F_m ; (3) n

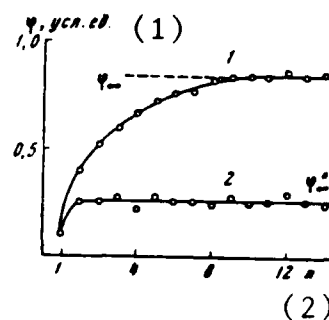


Figure 2. The relationship of the electric field potential on the number of test cycles in the atmosphere (1) and in a vacuum (2)
Key: (1) ψ , standard units; (2) n

Saturation of the friction force at high rates of sliding is reached more rapidly than at slower rates (Figure 3, Curves 1, 2). This is connected with the increasing action of speed on the separation of charges during friction (Figure 3, curves 3, 4).

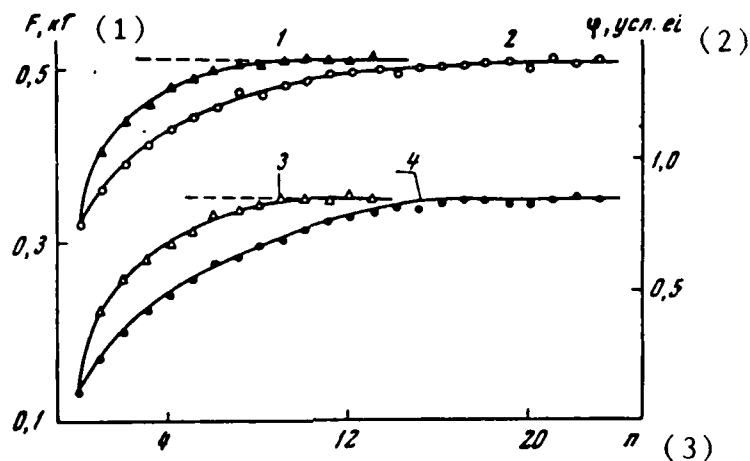


Figure 3. The relationship of the friction force F (curves 1 and 2) and the potential electric field ϕ (curves 3 and 4) on the number of testing cycles n : 1 and 3 - rate of sliding is 12 mm/min; 2 and 4 rate of sliding is 125 mm/min; standard load is 2 kg.

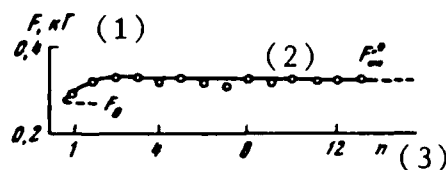
The matter of contact electrostatic charging was taken up in the reliable work of Deryagin [10,11]. In these works it was shown that when any two bodies are in contact, both metallic and nonconductors, at their interface there arises a dual electric layer; and for separation of such surfaces it is necessary to accomplish work against the force of the electric field, proportional to the density of the electric charge (σ) and the square of the potential difference (U^2).

However, the mechanism of the appearance of the contact potential different at the interface of bodies in contact at rest and during sliding are different. The possible reasons for the appearance of the difference in potential during friction are noted in Dubinin's work [2,3], and in that of Leonard and Leob [4].

The total contact surface in the friction process can be shown as a collection of faces of elemental charged condensers, overcoming the forces of the electric field of which requires an expenditure of work in the process of tangential displacement. However, the interaction of the charged surfaces acts as an additional load. In this way, besides the molecular interaction, acting on the actual contact surface, there is also an electrical interaction on the whole surface of nominal contact.

Figure 4. The relationship of the force of friction (F) of polymethylmethacrylate and steel on the number of test cycles (n) in a vacuum; the rate of sliding is 125 mm/min, and the standard load is 2 kg.

Key: (1) F, kg; (2) F_{∞}^* ; (3) n



Testing in a vacuum of 10^{-3} mm showed that in this case there is observed an insignificant increase in the friction force, which rapidly accumulated to the value of F_{∞}^* , which is practically equal to F_0 (Fig. 4).

Under vacuum conditions the surfaces of the friction pair also become charged. But the relationship on the Townsend discharge in the vacuum keeps the limit of increase in the difference in potential. In Fig. 2 we present the relationship of the potentials in vacuum conditions. The value of ϕ_{∞}^* in a vacuum is much less than ϕ_{∞} in the atmosphere. The amount of potential difference in charge (U), in accordance with the known Paschen's Law, depends on the work of gas pressure p on the charge gap h:

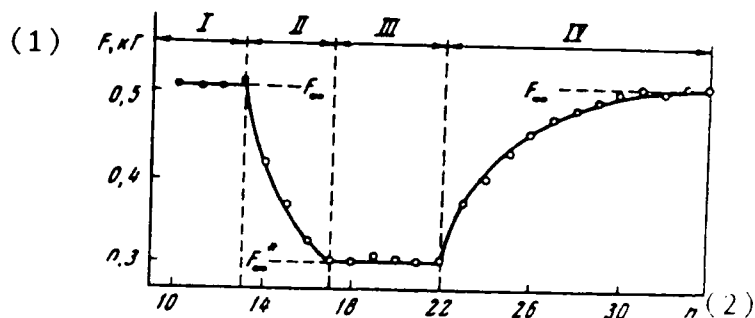
$$U = \frac{Bph}{[C + \ln(ph)]}$$

where C and B are constants, depending on the nature of the gas and the substance of the electrodes.

Figure 5. The relationship of the force of friction (F) of polymethylmethacrylate on steel on the number of test cycles n:

I - atmosphere; II - moment of separation; III - vacuum; IV - atmosphere; the rate of sliding is 125 mm/min; the standard load is 2 kg.

Key: (1) - F, kg; (2) n

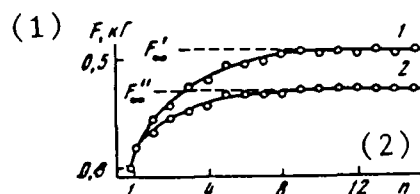


Paschen's Law works both for similar and for dissimilar fields which have the geometry of the discharge intersection [4].

To the extent that the increase in the force of friction with the number of test cycles is connected with an increase in the potential ϕ up to the value ϕ_{∞} , and ϕ_{∞} decreased with a decrease in pressure, so the force of friction must fall with an increase in pressure. In checking this we conducted the following tests. After obtaining the maximum attainable value for the friction force F_{∞} , the air was evacuated from the chamber and at that time we measured the force of friction. As the number of test cycles increased, with a constant decrease in pressure in the chamber to 10^{-3} mm, there was observed an even decrease in the force of friction from F_{∞} to F_{∞}^* (Fig 5).

Figure 6. The relationship of the force of friction (F) of polymethylmethacrylate on steel on the number of test cycles (n) at various temperatures: 1 - 20°; 2 - 80°; with rate of sliding of 125 mm/min and standard load of 2 kg.

Key: (1) F , kg; (2) n



In this way, if the research is begun in a vacuum, they during the first test cycles there takes place the accumulation in charge as is retained for the subsequent cycles.

The presence of a gas charge, which accompanies the friction, was noted in many investigations [2-5], and for cases of friction fluctuation as in Deryagin and Smilga [1].

Figure 6 presents the relationship of the force of friction on the number of test cycles at a constant rate of sliding at 20 and 80°. With an increase in temperature, F_{∞} decreases, $F_{\infty}'' < F_{\infty}'$. Probably the disorienting action of thermal movement with the increase in temperature leads to a decrease in the polarization of the polymer and a weakening of the effective electric field, resulting in a decrease in F_{∞} as the temperature increases.

We express our gratitude to Professor G.M. Bartenev for his attention to this work.

CONCLUSIONS

1. With an increase in the number of test cycles during back and forth movement of polymethylmethacrylate on a metal, the force of friction in atmospheric conditions increases up to an established value. Growth in the force of friction is connected with the electrolyzation of the friction pair to an established intensity.

2. In a vacuum, as a result of electrical charge, the established intensity of electrostatic charge is much less than in the atmosphere, so in these conditions the increase in the force of friction is almost not observed.

3. The electrostatic charging of the friction pair, which increases with sliding the polymethylmethacrylate along the metal, has significant influence on the value of the force of friction.

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