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### RESEARCH OF PROPERTIES CHANGES AND SURFACE MICROSTRUCTURE FILM BINDERS ON MODIFICATIONS MIXTURE OF FULLERENES

Changes of properties and structure of styrene-acryl film-forming polymer are investigated at its modification by a mix of carbon fullerenes. The interrelation between change of a superficial tension of solutions of polymer and change of a roughness of a surface of the cured films at modification is found. Physic-mechanical properties of new composition of mastic for processing of a surface of metalwork are defined. Recommendations are developed and practical approbation of finished goods for sealing of seams of construction designs is carried out.

**Introduction.** During outdoor work for sealing the outer surfaces, seams and joints of different constructions of buildings and structures, as well as the outer surface waterproofing of building structures, tanks, pipelines using special polymer mastic. However, resistance to cracking during operation of the existing trademarks such small film pastes. Application Technology of most of these compounds also has a number of disadvantages associated with the technology of their application, namely: large complexity and duration of works, the need for heat treated surfaces, instability insulation properties during storage and after drying, as well as insufficient stickiness to dirty surfaces.

Selection and use of sealant or mastic to fill construction joints allows virtually fully insulated space, with sealant and mastic should be as environmentally friendly and inexpensive desirable. Restoration interpanel seams wall constructions always passes with visible wall housing and almost always manually. For repair welds can use any materials, but experience has shown that it is optimal to use a combination of polyurethane and acrylic sealants. Best joint sealant, exterior-facing – polyurethane. Using acrylic sealant provides guaranteed adhesion to a variety of building materials and the ability to work with almost any weather.

Thanks to the excellent decorative properties and plasticity of acrylic mastic materials based on them are used primarily for the final work. Acrylics, mastics and sealants well fill all volumes. The main application of acrylic compositions - is still sealed or inactive compounds. Having excellent adhesion to such materials as concrete, masonry, wood, and plaster, acrylic-based sealants are good for plugging various problem areas. This gap between the sill and the wall, local cracks in concrete or brick walls, cracks in the dried-out wood panels or boards, slit by contiguity wooden window frames to a wall opening. Acrylic sealant rather long retains its elasticity, can withstand heavy vibration and is easy to color and plaster-

ing. Especially convenient to plug them shallow holes and cracks - just poured sealant inside and dries to form a surface that can be easily further finishing work.

Earlier studies [1, 2] of the possibility of creating polymer compositions with improved performance characteristics were run by modifying nanomaterial.

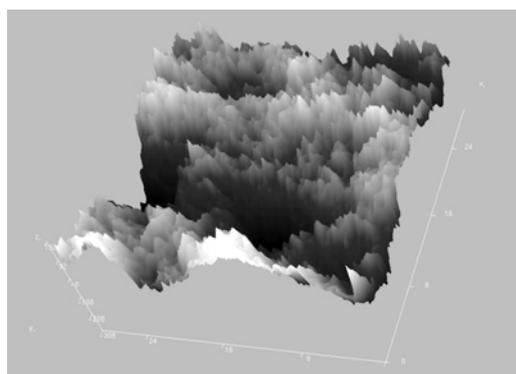
Purpose - to assess the possibility of creating a film-forming polymeric material with improved technological and operational characteristics.

**Main part.** In this study, tests were conducted one-component visco-elastic mastic based film forming styrene acrylic copolymer organomodified carbon nanomaterial fullerene series. As the starting polymer is selected brand styrene acrylic copolymer Akrokam-23 dry polymer content of 56 % of the residue, the mixture was chosen modifier carbon fullerene C50-C92 fraction, with the following ratio of components in the mixture: C<sub>50</sub>-C<sub>58</sub> (14.69 %), C<sub>60</sub> (63.12 %), C<sub>62</sub>-C<sub>68</sub> (5.88 %), C<sub>70</sub> (13.25 %), C<sub>72</sub>-C<sub>92</sub> (3.06 %). Akrokam-23 and fullerene mixture equally well dissolved in toluene, so the preparation of compositions with different concentrations of modifier and optimization of content components were quantified by conventional methods. It should be noted that the introduction of a solution of a mixture of fullerenes causing discoloration of the composition due to the yellow-brown solution of the starting dye product. Characteristics of the starting Akrokam-23 product are given in Table 1.

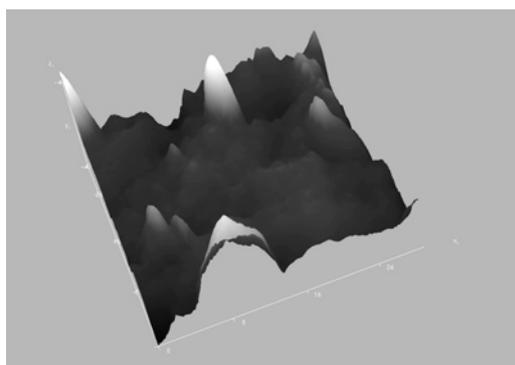
Table 1  
**Technical characteristics of copolymer Akrokam-23**

Index name	Value
Color by iodometric scale, mg J/100 cm <sup>3</sup> , not above	10
Dry residue, %, within	48-56
Relative viscosity at a temperature of (20 ± 0,5) °C by viscometer VZ-246 with a nozzle diameter of 4 mm, within	60-190

To assess changes in the surface properties of the resulting formulations with varying concentrations of a mixture of fullerenes in a range from 0 to 0.03 phr (dry residue), measurements were made of the surface tension on the instrument du Nui, which showed gradual reduction of surface tension with increasing concentration of the mixture of fullerenes. Analysis of the relevant changes in the physical and mechanical properties of the film-forming copolymer by modification of the fullerene mixture showed that the optimal value of the concentration of carbon modifier observed phenomenon reducing the surface tension of the film  $10 \text{ N/m}^2$ , which confirms our hypothesis previously put forward by “smoothing” of the surface film coating for visual confirmation of which were carried photographs of the surface of the films by scanning probe microscopy tool “Nanoeducator”. Micrograph (Fig. 1) was confirmed by a sharp decline in the roughness of the films.



a



b

Fig. 1. View of the surface of the films before modification (a) and after modification (b)

“Smoothing” sample surface with a corresponding decrease in the resulting shrinkage of the film forming property of the composition is valuable as stickiness to the surface processing and improving its opacity, leading to a decrease in the flow of mastic per unit surface area.

To determine the structure of these rubbers used method FTIR spectroscopy attenuated total internal reflection (FTIR) in the variant with 10-fold beam passing through the sample and the ATR crystal. The study was carried out on FTIR spectrometer NICOLET 6700. The selected spectral range was from 400 to 4,000  $\text{cm}^{-1}$ . For registration of the optical characteristics using a monolithic polymer thick film of rubber of about 20 microns, the aluminum substrate obtained from 1 % solutions in toluene. Oxidation was carried out at low temperature films laboratory furnaces SNOL 58/350 at a temperature of  $100^\circ\text{C}$  for 24 hours. Samples dependent on the type of analyte processing of butadiene rubber are given in Table 2.

Table 2

**Investigated samples  
of the polymer Akrokam**

Sample number	Sample name and type of treatment
1	Commercial rubber film (control)
2	Commercial rubber film which has been subjected to heat treatment
3	Film commercial rubber modified by mixture of fullerenes $\text{C}_{50}$ – $\text{C}_{92}$ groups
4	Film commercial rubber modified by fullerene mixture of $\text{C}_{50}$ – $\text{C}_{92}$ groups, subjected to heat treatment

Typical spectra of polymer samples are shown in Fig. 2.

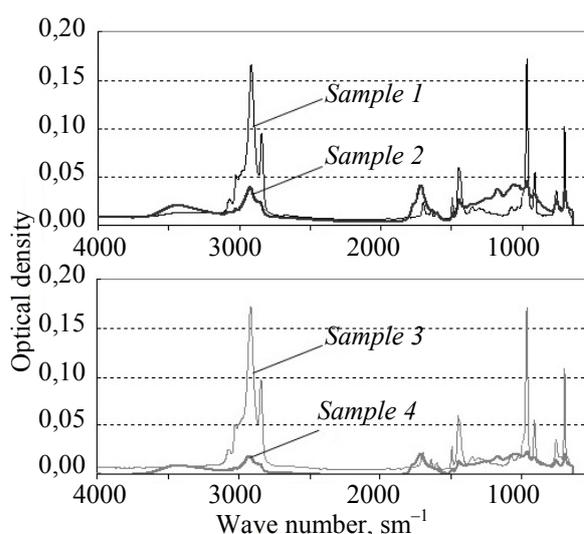


Fig. 2. The characteristic spectra of samples

As seen from Fig. 2, differences in the spectra of samples 1 and 3 is insignificant. As a result of

heat treatment the increase in the intensity of the hydroxyl absorption band ( $3640\text{ cm}^{-1}$ ) and carbonyl groups ( $1720\text{ cm}^{-1}$ ) with a simultaneous decrease in the intensity of the other portions of the spectrum, as shown by the samples 2 and 4. This indicates to join oxygen. It should also be noted reduction and change in intensity of the absorption bands of the investigated polymer-modified fullerene, heat-treated (Fig. 2, sample 4). Due to the fact that the spectra are characterized by the relative convergence, for a more detailed study of the results is necessary to conduct analysis of variance.

Processing of the spectral data were based on one-way ANOVA, which revealed features of chemical reactions and processes related to changes in the structure of polymers under the influence of modifier and aggressive factors such as thermal effect. Data processing was carried out by relevant categories plots obtained IR spectra, as shown in Table 3.

Table 3

Categories portions of the spectra

Group (types of oscillations)	Wave number, $\text{sm}^{-1}$
Deformational $\text{CH}_2$ in vinyl	from 904 to 995
Scissor in $\text{CH}_2$ , $\text{CH}_3$	from 1406 to 1429
Valent $\text{C}=\text{C}$ in conjugated systems	from 1593 to 1649
Valent $\text{C}=\text{C}$ without conjugation	from 1650 to 1701
Valent $\text{C}-\text{H}$ в $\text{CH}$ , $\text{CH}_2$ , $\text{CH}_3$	from 2974 to 3061
Valent $\text{OH}$ and $\text{H}$ bond	from 3128 to 3745
Valent $\text{C}=\text{C}$ and deformational $\text{H}_2\text{O}$	from 1554 to 1884

Processing performed spectroscopy method of least squares means. Comparing the data in Fig. 2 (samples 1 and 2), we can see that there is a statistically-significant difference in the spectra, ie, significant changes in the spectra in this case is not revealed. The spectra of the samples 3 and 4 are similar in shape, but the difference was statistically significant. For sample 4, the last processing of all types is characterized by suppressing the intensity fluctuations of all kinds. Data analysis of samples 1 and 3 reveals a strong suppression of the valence vibrations of the  $\text{C}-\text{H}$  in the methyl, methylene and methine groups outside junction deformation in  $\text{CH}_2$  and the emergence of bands hydration. Heat treatment and modification of fullerenes lowers the intensity of all modes, including a system with  $\pi$ -conjugation. Reducing the amount of  $\text{C}-\text{H}$  vibrations in the hydrocarbon polymer unit may be ex-

plained by steric effects due to the closer packing of the polymer units and blocks the growth of polymer molecular weight. But decrease is observed for sample 3 investigated rubber-modified mixture of fullerenes  $\text{C}_{50}-\text{C}_{92}$  group, although heat treatment also leads to a marked decrease in vibrations of the carbon - hydrogen.

Thus, in the test group samples rubber Akrokam effects trademark "hydration" are shown for all samples except sample 3 commercial rubber-modified fullerene mixture. "Draining" effect modifier can be administered in the sorption properties of fullerenes: Tap on the surface of the water molecules through hydrogen bonds with the  $\pi$ -conjugated five-membered ring system of the fullerene with subsequent desorption during drying. Fullerenes are added to the polymer is likely located on the surface thereof, its interacting  $\pi$ -electronic system with  $\pi$ -electrons of the benzene styrene structure.

As a result, production testing of an experimental batch of products for construction work was to determine the actual flow rate in the modified mastic sealing joints and seams interpanel. He was  $0.20-0.35\text{ kg/rm. m}$  (including drying shrinkage), formed the actual conditional joint width was  $30\text{ mm}$ , the conditional filling depth –  $3\text{ mm}$ , which is significantly lower than the existing building standards.

Further, in comparative tests of coatings applied on the concrete wall of the building, in vivo atmospheric aging (south side, August – November), it was shown that the time until the first crack of the modified coatings increased almost in three times that obtained confirm data early on stabilization of fullerenes process thermal aging diene polymers [3].

Because acrylic sealants are one-component formulations, can be used immediately after opening. They are harmless to humans and animals, are non-toxic, and do not cause skin burns and fire-safe. So when working with acrylic sealant, it is not necessary to ventilate the room and use gloves or respirator. When subjected to tensile strain acrylic sealant exhibits elasticity. The magnitude of irreversible deformation is more than  $50\%$  of the working area of the sample. The amplitude of deformation during its operation does not exceed the maximum ten percent elongation. If acrylic sealant is used for internal works, its tensile properties play no special role. For exterior preference should be given more resilient sealing materials, since the smaller the rigidity of the sealant depends on the temperature variations, the above frost compound.

When temperature fluctuations environmental acrylic sealant retains all its properties, including the remains flexible and provides reliable contact

with the materials. The optimum operating temperature of acrylic sealant is in the range of temperatures from  $-20$  to  $+70^{\circ}\text{C}$ . Only in this temperature range, the sealant can withstand numerous cycles of freezing and defrosting and ensures the integrity of the weld while it is better not to use acrylic sealant is heated space, since it is possible delamination from the substrate material.

**Conclusion.** The results of studies on the modification of styrene acrylic copolymer mixture of carbon fullerenes confirmed the earlier results on the integrated effect of carbon nanofillers on the properties of diene polymers. Thus, modification of new copolymers styrene acrylic fullerene mixture fraction  $\text{C}_{50}\text{--}\text{C}_{92}$  allows the temperature range from  $-40$  to  $+40^{\circ}\text{C}$ , and improve the weatherability without deteriorating the durability of the coating adhesion to metal and concrete, wherein the encapsulation operation can be performed without first cleaning the surface. If necessary, the resulting surface sealed film can hold all kinds of painting exterior paints.

## References

1. Игуменова, Т. И. Модификация клеевых композиций на основе бутадиен-стирольных каучуков наносоединениями углерода / Т. И. Игуменова, А. В. Чичварин // Образование, наука, производство и управление: сб. тр. / Старооскольский технол. ин-т. – 2011. – Т. II. – С. 29–31.
2. Чичварин, А. В. Явление стабилизации теплового старения связующих на основе товарного полибутадиена смесью фуллеренов группы  $\text{C}_{50}\text{--}\text{C}_{92}$  / А. В. Чичварин, Т. И. Игуменова // Вестник Белгородского государственного технологического университета им. В. Г. Шухова. – 2011. – № 4. – С. 142–144.
3. Чичварин, А. В. Термоокислительная деградация полибутадиенов под влиянием смеси фуллеренов группы  $\text{C}_{50}\text{--}\text{C}_{92}$  / А. В. Чичварин, Т. И. Игуменова, М. А. Гудков // Фундаментальные исследования. – 2012. – № 11 (часть 1). – С. 202–205.

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