Influence of lead-manganese naphthenate on changes in the dynamic edge wetting angle upon spreading of styrene-acrylic dispersion

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Abstract. The effect of lead-manganese naphthenate on the change in the dynamic contact angle during spreading of a styrene-acrylic dispersion is studied. The dependences of the change in the dynamic contact angle in time are obtained for various concentrations of lead-manganese naphthenate in solution. As a result of the analysis of the experimental data, a concentration region was revealed in which the dynamic wetting angle varies in the widest range with the lowest speed compared to solutions of other concentrations. The results of the research will be used to optimize the composition of the polymer-mineral composite material and will make it possible to obtain a polymer matrix that most wets the mineral fillers, and the resulting composite will have the greatest mobility and vitality.

1. Introduction

The development of the market of construction and outfitting materials requires the search and development of new materials with improved operational and technological properties.

Recently, polymer-mineral compounds for repairing cement coatings [1], road paving [2] and self-leveling floors [3] are in high demand by consumers. Due to its excellent properties - increased density, strength, high modulus of elasticity, high abrasion resistance, good slip resistance, impact strength, thermomechanical, optoelectronic and magnetic properties, fire resistance, polymer-mineral composites are considered as promising modern materials [4].

One of the urgent tasks when creating polymer-mineral composite materials is to ensure the effective hardening while maintaining the mobility of the mixture during its laying. The development of such compositions is possible only with careful selection of all components of the formulation and an extensive study of its aggregate impact [5, 6].

The range of polymer additives used in the formulation of polymer-mineral and polymer-cement compositions is quite wide. The most popular are acrylic latexes or styrene-acrylic dispersions, which have high adhesive properties to various materials, and are also capable of forming elastic vapor-permeable coatings with high light and weather resistance. Due to the small size of the particles (50 - 100 nm), dispersions run deep into the porous base, strengthening it.

The study of the dynamics of changes in the contact angle is widely used in research practice: in assessing the effectiveness of the destruction of oil-water emulsions [7], in studying the effects of impregnation of porous bodies with liquids [8], etc.

The authors indicate a significant effect of the structure and properties of the substrate, the composition and properties of the spreading liquid on the nature of the change in the dynamic contact...
angle. An important fundamental task is to study the dynamic processes that occur in complex polymer systems during their hardening and polymerization in the presence of substances that accelerate these processes.

When applying coatings based on aqueous dispersions of polymers, during their hardening, complex interrelated processes of water evaporation, polymerization, film formation and coalescence of the dispersed phase occur. To accelerate the surface of the polymer-mineral coatings polymerization time, auxiliary substances – siccatives are used. The most widespread are siccatives which are based on the salts of naphthenic acids of lead, cobalt, manganese, calcium, zinc and iron. They affect the rate of formation and decomposition of hydroperoxides, change the amount of oxygen, which determines the kinetics of the formation of the crosslinked structure, and, consequently, the properties of the coatings.

Studying the laws of spreading of drying and, at the same time, coalescing polymer dispersions, establishing the effect of the composition of such dispersions on their behavior when wetting surfaces, will allow them to purposefully control their properties by reasonably introducing functional additives. As part of optimizing the compound of the polymer-mineral composite material [9], the research of the effect of lead-manganese naphthenate on the change in the dynamic contact wetting angle when the styrene-acrylic dispersion spreads were conducted. The aim of the paper is to determine the effect of siccative additives on the spreading of styrene-acrylic dispersion on a solid surface and the choice of its optimal amount.

2. Materials and methods of research

Styrene-acrylic dispersion is the most effective component of polymer-mineral composites [9, 10], due to the complex of increased properties such as physicomechanical, technological and operational ones.

Styrene-acrylic aqueous dispersion is a product of the emulsion polymerization of styrene, acrylic acid and butyl acrylate. The dynamic viscosity of the dispersion was 1.3 Pa·s, the mass fraction of non-volatiles was 50 ± 1%, and the size of particles did not exceed 90 nm. During the research, the Akratam AS 05.1 dispersion, commercially available from industry, was used.

The choice of lead-manganese naphthenate to accelerate the formation of styrene-acrylic dispersion was chosen due to its advantages in the synergistic action of the components: lead ions had catalytic activity to the oxygen absorption reaction, while manganese ions accelerate the polymerization reaction [10]. During the research, the NF-1 siccative was used, which is a solution of lead-manganese naphthenate in white spirit.

The dynamics of film formation and hardening of the mixtures were studied by video recording the transient process of spreading a polymer drop on the glass surface using a DigiMicro digital microscope, followed by computer processing of the video sequence in VideoPad v6.32 and determined the contact angle used the capabilities of MicroCapture v2.0. The droplet volume was 0.2 ml. Studies were carried out at the temperature of 20±0.1°C. For each moment of time, three measurements of the angle \( \theta \) were carried out, after which the mathematical expectation and the standard deviation were determined.

The research methodology included the following main steps as dosing and mixing the components (styrene-acrylic dispersion and lead-manganese naphthenate), applying a mixture drop to the glass surface, video recording of the drop spreading process prior to computer processing of the video sequence and measurement of the dynamic contact wetting angle. Then we repeated the steps for predetermined concentrations of lead-manganese naphthenate in a styrene-acrylic dispersion. Finally, the work was finished by the construction and analysis of the dependence of changes in the dynamic contact wetting angle over time with variation in concentration patterns.

The range of concentration of siccative during the research (0-8% of the total mass of the dispersion) was selected based on the practice of using lead-manganese siccative additives, as well as the recommendations of operating companies. The solutions were prepared by mechanical mixing of the styrene-acrylic dispersion and desiccant used a propeller stirrer at speeds not exceeding 20 s\(^{-1}\).
3. Results and discussion

In figure 1 photographs of drops at instant times corresponding to the beginning (t = 0) and end (t → ∞) of spreading are shown. When droplets was applied to the glass surface, the contact angle when wetted with a mixture with a desiccant concentration of 5% is of the greatest importance among all the studied mixtures with concentrations from 0 to 8%. The change in the contact angle over the entire spreading period for mixtures with a low concentration of lead-manganese naphthenate (for example 1%) occurs by a smaller value compared to high concentrations (5-8%).

![Figure 1. Drops of mixtures at the initial (t=0) and final (t→∞) spreading stages for 1, 5 and 8% of syccative concentration.](image)

![Figure 2. Changing of the dynamic wetting angle (θ, degrees) in time (t, s) for 1, 5 and 8% of syccative concentration, where I and II are spreading areas with various prevailing forces.](image)

The figure 2 shows the graphs over the time of the average value wetting angle while spreading of the drops of mixtures with concentrations of lead-manganese naphthenate 1, 5 and 8% (standard deviation does not exceed 0.5°). On the graphs of the change in the wetting angle over time (figure 2), two distinctive sections can be distinguished (indicated by the numbers I and II), which, depending on the concentration, have different lengths. The average speed of change of the angle θ in section I is more than 10 times higher than the speed in section II. To explain this difference, it is necessary to analyze the forces acting in the process of spreading the drop.

The process of spreading of a drying and coalescing liquid is nonequilibrium. In figure 3 there are the forces in a three-phase “gas-liquid-solid” system when a drop of a viscous liquid spreads over a solid surface. When it spreads, the gravity of the liquid, which is conducive to the spreading, decreases due to moisture evaporation; the force of viscous resistance increases due to the coalescence of polymer particles; the interphase tension at the “liquid-gas” and “solid–liquid” interfaces increases with the raising of surface tension of the liquid phase, but the strength of the interphase tension at the “solid-gas” interface remains constant with fixed parameters of the solid and gas phases.

![Figure 3. Driving forces of the process of spreading drops on a solid surface.](image)
According to the existing views on the physicochemical features of the wetting and spreading of a liquid drop over the surface of a solid material [11], the driving force of the nonequilibrium spreading process is determined as

\[ F_{ms} = F_{s-g} + kF_G - F_{ls} - F_{dl} - F_\eta, \]

where \( F_{s-g} \) – interphase tension force at the “solid-liquid” interface; \( F_{s-g} \) – interphase tension force at the “solid-gas” interface; \( F_{ls} \) – force (projection of force on the horizontal axis) of interphase tension at the “liquid-gas” interface; \( F_G \) – gravity; \( F_\eta \) - the force of viscous resistance; \( k \) – coefficient which takes into account the influence of gravity on the spreading process.

An analysis of the results of experimental studies of the dynamics of the change in the wetting angle depending on the concentration of lead-manganese naphthenate in the solution showed that in the range of concentrations of 5-6.5%, the dynamic wetting angle varies in the widest range, while its rate of change is the highest in comparison with solutions of other concentrations.

In the case under consideration, when the spreading of a drop is accompanied by the evaporation of water and the coalescence of polymer particles, the acceleration of spreading occurs only with an increase in the interphase tension at the “solid – liquid” interface.

In section I, interphase tension forces make the largest contribution to the spreading of the drop. The change in the spreading rate is owing to the dynamics of the forces \( F_{ls} \) and \( F_{s-g} \) from their initial values, depending on the amount of syccative used. The spreading is accompanied by significant change in surface tension. According to the authors, this occurs as a result of the transfer of oxygen in the film-forming substance, which reduces free surface energy particles of the dispersed phase and initiates the process of coalescence, while interacting with film-forming methylene groups.

Due to the effect of the optimally selected amount of added lead-manganese naphthenate (~ 5%) at the initial stage of spreading, the surface tension of the solution increases by 25% comparatively the mixture with 1% naphthenate additive, while the rate of change of the wetting angle decreases by 16%, which allows the solution maintain its mobility and moisten hard surfaces for a longer time.

In section II, the change in the spreading rate is owing to the effect of the force of viscous resistance, the increasing rate of which is determined by the coalescence of polymer particles. The length of the time interval of the effect of viscous resistance forces (section II) in the case of having an optimally introduced additive of lead-manganese naphthenate decreases by 30%, and the spreading rate decreases by 60%.

Conclusion
The salts of heavy metals of naphthenic acids are widely used in the technology of paints and varnishes of air drying as film formers. In this work, for the first time, the dynamics of hardening of a drying and coalescing styrene-acrylic dispersion, used as a matrix of a new polymer-mineral composite material with enhanced adhesive properties, was studied.

The nature of the change in the dynamic wetting contact angle over time was established as a result of experimental studies of the spreading of evaporating and coalescing drops of styrene-acrylic dispersion with the addition of lead-manganese naphthenate.

It is shown, that the curves of transition process have the form that is common for aperiodic second-order link, which indicates parallel and sequential course of several processes. The transition process of changing the contact angle during spreading of a styrene-acrylic dispersion with the addition of a desiccant can conditionally be divided into two stages which include the spreading under the influence of interfacial tension and spreading due to the action of the force of viscous resistance.

The studies conducted in the work allowed the authors to make a reasonable choice of the amount of desiccant introduced into the composite material, which will allow at the initial stage to increase the film formation time necessary for successful work on applying the composite to the substrate, and at the final stage to increase the coalescence rate of the particles, which determines the curing time of the formed coating.
The results of the study can be used to optimize multicomponent polymer-mineral compositions to substantiate the amounts of added additives and to phenomenologically explain the mechanisms of their influence on the ongoing processes.

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