

*Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 80th anniversary*

AQUEOUS ECOLOGICAL INTUMESCENT FIRE RETARDANT COATINGS FOR MULTIFUNCTIONAL APPLICATIONS.

1. PREPARATION AND CHARACTERIZATION

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Aqueous ecological intumescent fire retardant coatings for multifunctional application having as basic components for char formation the common commercial compounds ammonium phosphate or polyphosphate, pentaerythritol and melamine and titanium dioxide as pigment were obtained. Inorganic charges (kaolin, tri-hydrated alumina, organically modified bentonite and sodium one) and carboxymethylcellulose were introduced to increase the adherence to different substrates, cohesion of films, decrease the permeability at gases, favour the formation of a rigid spinel structures by combustion in combination with titanium dioxide, increase stability and impart the rheological characteristics required by the method of application. They were characterized by dry substance contents, dynamic viscosities, aspect of dry and wet films, grid adherences, expanding indices in laboratory conditions and aspect of the formed solid foams. The most effective intumescent system is that containing ammonium phosphate and carboxymethylcellulose, followed, in the decreasing order of expanding indices, wet and dry film properties, adherence to supports and easiness of application by brushing by that containing ammonium phosphate and tri-hydrated alumina, the one that contains ammonium phosphate and kaolin, that only with ammonium phosphate and the composition that contains ammonium polyphosphate and kaolin.

INTRODUCTION

When exposed to fire, all commonly used structural materials lose a part of strength, depending on their nature and temperature: steel first expands with increasing heat, but above its critical temperature (about 540°C) starts to lose its load bearing capacity (about 75% at 600°C), concrete cracks and spalls, timber depletes by charring.¹

The lack of fire resistance of structural materials produces great damages and expenses. Thus, over 395,000 home fire damages were produced and 3,030 civilians died in 2005 in U. S. A., totalizing more than 6.7 billion dollars.^{2,3}

Fire retardants are commonly used in fire fighting. They are compounds that help to delay or prevent combustion and can operate both by physical and chemical actions.¹

Physical actions by which retardation of combustion can be done are: (a) cooling – some chemical reactions cool the material down; (b) forming of a layer that protects the remaining material; (c) dilution – some retardants release water and/or carbon dioxide while burning, that may dilute the radicals in the flame sufficiently enough for it to go out.

Retardation of combustion by chemical actions can be realized by: (a) reactions in the gas phase – reactions in the flame (i.e. gas phase) can be interrupted by fire retardants, but this type of retardants use halogens (bromine and chlorine) and usually the released gas are dangerous; (b) reaction in the solid phase – this kind of flame retardants melt and flow away from the flame, but the resulted droplets are flammable; (c) char formation – solid phase flame retardants produce a layer of carbon char on surface that burn more difficult,

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preventing further burning; (d) intumescent – which induce thermal expansion of the protecting material. Such retardants react when they are heated, building up a swollen multi-layered insulating structure able to provide much better protection.⁴ They can be added to plastics, or can be used as coating/paint, tape, caulk/sealant, and putty.⁵ Intumescent coatings are also called passive fire protection systems.

Traditional intumescent flame retardant coatings contain four main components that are the basic elements for char formation:^{6,7} a source of carbon or carbon donor, a source of acid or acid donor, a source of gas or blowing agent and a binder to maintain all the components suspended in dispersion medium and form a solid film on surface. It swells under the action of heat, forming a thick porous layer of char that perfectly insulate the substrate against the excessive increase of temperature.⁸ It was demonstrated that the binder takes part also in the control of char expansion, assuring an uniform structure of the solid foam.⁹

Depending on the mechanisms of acting, more types of intumescent coatings can be distinguished.^{10,11} Interacting distinctly with various surfaces on which are applied, they are specific for the substrates for which were designed.

From the statistics it is known that more than 90% of the lives claimed by fire are not caused by the flames but by the emission of toxic and corrosive gases.¹² Thus, environmental and health hazards as well as fire safety, such as smoke density, smoke toxicity and corrosion, low toxic gas emission, are imposed to intumescent compositions.

The object of this paper is the preparation and characterization of some aqueous intumescent fire retardant coatings based on commercial components, designed to combine ecological and fire safety requirements with multifunctionality, i.e. the ability to protect surfaces of materials (metals, plastics, concrete) used in different industrial fields like energy, construction, transportation, etc.

EXPERIMENTAL

Compounds: ammonium phosphate and ammonium polyphosphate II (degree of polymerisation higher than 1000, branched chain, decomposition temperature higher than 350°C); pentaerythritol (Hercules, USA); melamine (Azomureş, Roumania); titanium dioxide rutile, particle size 25-30 µm (Agrofert Czech Republic); tri-hydrated alumina with low sodium content obtained by ICEMENERG, average diameter 1-5 µm; organically modified calcium bentonite (montmorillonite) Luvogel 7, particle size x 50 cca 15 µm (Lehman&Voss); sodium bentonite (Medieşu Aurit, Roumania); kaolin, particle size under

63 µm (Harghita, Roumania); carboxymethylcellulose (Walogel, Bayer). The products were used as received.

The intumescent aqueous dispersions were obtained either by advanced grinding into a porcelain pot mill or using a laboratory disperser. Their concentrations ranged between 45.54% and 69.23% as shown in Table 1.

Methods of characterization: The following characteristics were determined: (a) stability, by measuring the heights of sediments during 15 weeks; (b) rheological behaviour at $25 \pm 0,1^{\circ}\text{C}$ using a Haake VT 550 viscotester, developing shear rates ranging between 3 and 1312 s^{-1} ; (c) - drying time at $15\text{-}20^{\circ}\text{C}$ and 65% relative humidity for two layer films 400 µm thick; (d) adhesion at different supports, according to SR EN ISO 2409:2003; (e) - passivating effect, by inspecting the aspect of two layer coats of intumescent material applied on scrubbed (gentle brushing), degreased and dried rusted low alloy steel OL 37; (f) - expanding indices of the two layer coats deposited on low alloy steel OL 37 dried for 24 h, cut in 4-10 mm² pieces and burned in laboratory conditions using an alcohol lamp.

A number of 34 aqueous intumescent compositions containing as basic components for char formation ammonium phosphate or polyphosphate, pentaerythritol and melamine and titanium dioxide as pigment were prepared. The ten selected systems are listed in Table 1 together with their content of dry substances, viscosities at zero shear rate, η_0 , or dynamic viscosity, film and char aspect and expanding indices.

Solutions' pHs was adjusted between 5.0 and 5.5 to assure the passivating effect and heat foaming of the intumescent compositions.

RESULT AND DISCUSSION

Intumescent coatings are fire protection systems used to protect flammable materials such as wood or plastic from fire (prevent burning), but also to protect steel and other structural materials from the high temperatures of fires (prevent or retard structural damage during fires).¹³ They apply to a surface like a paint and are designed to expand when subject to heat to form an insulating and fire-resistant covering. Given their advantages over the other forms of passive fire protection:¹⁴ (a) relative ease of application and durability; (b) keeping of weight of fire protection to minimum, allowing to achieving greater spans; (c) taking up of very little space compared to other forms of passive fire protection; (d) time and cost savings due to off-site application; (e) more scope for services design; (f) ability to overcoat the intumescent layer with a decorative sealing coat; (g) easily repaired if damaged; (h) reduction in intumescent thickness due to the advanced fire engineering; (i) the self-healing nature of the damaged intumescent char, that means a minimum reduction in overall performance, making them ideal for a whole life protection, they are extensively used today. Additionally, they do not require independent activation or electrical power to function, hence never fail to work.¹⁵

Table 1

Selected intumescent compositions, content of dry substances, viscosities, wet and dry film aspects, expanding indices and appearance of the formed solid foam

Composition	Dry substance, %	η_0 , mPa.s	Aspect of wet film	Aspect of dry film	Grid adherence	Expanding index, %	Aspect of char
a	60.00	4600.87	Good spreading, homogeneous film	Homogeneous, continuous	0	795.0	Continuous expanding, dense, high volume foam
a-CMC	50.00	1238.39	Good spreading, homogeneous film	Homogeneous, continuous	0	1091.3	Continuous expanded, very high volume, dense, very adherent foam
b	67.15	1665.87	Good spreading, homogeneous film	Rigid	1	450.6	Dens expanded layer, with good edges
b-CMC	53.49	-	Non-homogeneous	Friable	3	613.0	Friable, open pores foam
1a**	65.22	6349.94	Homogeneous, good spreading	Homogeneous, breaking resistant	0	814.0	Continuous expanded, high volume, dense foam
1b	65.22	45.19*	Difficult spreading, non-homogeneous	Exfoliation tendency	2	495.4	Ovoid shape solid foam
1b-CMC	45.54	4230.60	Good spreading, homogeneous, very good aspect	Homogeneous, continuous, less friable than b-CMC	0	742.0	Continuous expanded, dense, high volume foam
2a	65.22	-	Cohesive film	Homogeneous, breaking resistant	0	936.8	Continuous expanded, very high volume, dense foam
3b	65.22	11134.39	Difficult spreading, brush traces seen	Exfoliation tendency, friable	2	578.2	Open pores, friable, ceramic aspect
4b	69.23	15248.10	Good spreading film	Homogeneous, breaking resistant	0	622.4	Continuous expanded, high volume, dense, very adherent foam

a – $\text{NH}_4\text{H}_2\text{PO}_4$; b – ammonium polyphosphate; 1 – kaolin; 2 – tri-hydrated alumina; 3 – Luvogel 7; 4 – natrium bentonite; CMC – carboxymethylcellulose; * – dynamic viscosity;

** – highest passivating effect

The four essential interdependent components specified in introduction have the following functions: the source of gas releases large amounts of non-flammable gas such as nitrogen, ammonia or carbon dioxide when heated, the source of acid releases an acid which chars the carbon donor – a polyhydroxilic compound – causing the hardening of layer of bubbles and giving a fire-resistant coating, the binder gives a viscous liquid that traps the released gas in bubbles and produces a thick layer of froth.^{6, 7} The binder can also be a carbon source when the polymer contains functional groups. In case of fire, the thick non-flammable layer of bubbles – that can be varied from a light and fluffy layer to a dense, crisp and quite solid honeycomb¹⁶ – effectively insulates the substrate from the rapid temperature increase that would otherwise occur in a fire.

The most widely used halogen-free or ecological flame retardants are the phosphorus-based ones.¹⁷ Among them, one should distinguish inorganic phosphates or polyphosphates.¹⁸

Certain nitrogen-containing compounds synergize the flame retardant action of phosphorus¹⁹ and are used in conjunction with phosphorous and polyol compounds.

The choice of components being of paramount importance due to their essential effect on the coating properties, rate of charred mass formation and its structure,⁸ the following compounds were selected to obtain the halogen-free intumescent fire retardant aqueous coatings for multifunctional applications in accordance with literature data: (1) ammonium phosphate or polyphosphate II as acid donor, the last one – being relatively water-insoluble – imparting improved durability to the coating,²⁰ (2) pentaerythritol that – due to its compact structure and high density of hydroxyl groups – is an effective carbon donor for intumescent coatings²¹, providing outstanding properties as good balance between the drying velocity, viscosity and water resistance of coating in normal conditions, short esterification time during the fire, large foaming ratios, entering the intumescent process at low temperature and maintaining it for a long time;²² (3) melamine as blowing agent, due to its advantages:²³ cost effective, low smoke density and toxicity, reduced corrosion, safe handling and environmental friendliness and (4) titanium dioxide as pigment. The last three compounds being common, they are not specified in Table 1.

Melamine enables also the creation of hard, glossy surfaces that are durable, hardwearing,

highly resistant to heat, chemicals and moisture, safe, hygienic, and non-allergic.²⁴ That is why it was used also as binder for the obtained intumescent systems. In this way the toxic gas emission from the organic polymers used as binders while burning is eliminated.

To increase the adherence to different substrates, cohesion of films, decrease the permeability at gases, favour the formation of a rigid spinel structure in combination with titanium dioxide by combustion and impart the rheological characteristics required by the method of application, inorganic charges as kaolin, tri-hydrated alumina, organically modified calcium bentonite Luvogel 7 and sodium bentonite were introduced. Spinel structure confers the aspect and consistency of pumice stone to the solid foam. To increase the viscosity, and thus the stability of aqueous dispersions, and improve the film-forming properties, carboxymethylcellulose was added to some compositions, as specified in Table 1.

All the dispersions settled down more or less in 15 weeks, but they can be easily re-dispersed by gentle stirring. The most stable are the dispersions containing CMC, as expected, due to the colloid protecting action of the polymer and increasing of viscosity.

A pH of 5.0-5.5 was necessary to assure the metal passivating: if it is lower than 5.0 the metal substrate is affected by suppressing the passivating effect, while one higher than 5.5 reduces the heat foaming effect due to the low level of the acid source in the system.

The passivating effect was established by inspecting, after one month, the surfaces of coating and metal after removing of coating. The metal surfaces were pretty clean, the best passivating effect having the composition 1a containing ammonium phosphate and kaolin due to the passivating effect of phosphate ions released by the ammonium phosphate, while all the others have satisfactory effect.

The studied intumescent systems have different rheological behaviour, dependent on their composition. Thus, 1b (that contains polyphosphate and kaolin), which has the lowest viscosity, behaves as an ideal plastic fluid onto the whole shear rate range (145-1312 s⁻¹); a-CMC (with phosphate and CMC), 1a (containing phosphate and kaolin) and 1b-CMC (with polyphosphate, kaolin and CMC), which are more viscous, have pseudoplastic behaviour; a (that contains phosphate), b (with polyphosphate) and 3b (containing polyphos-

phate and Luvogel 7) behave as pseudoplastic fluids at low shear rate and as ideal plastic at high ones; 4b (that contains polyphosphate and sodium bentonite) as ideal plastic fluid at low shear rates and as pseudoplastic at higher ones.

To exemplify the changing of behaviour from pseudoplastic to ideal plastic, the rheogram of system a is shown in Figure 1 (curve C): passing from pseudoplastic to ideal plastic behaviour takes place at a shear rates of about 450 s^{-1} . This suggests a slight continuous destructure of the dispersion under the action of shear stress until 450 s^{-1} and that the structure acquired at 450 s^{-1}

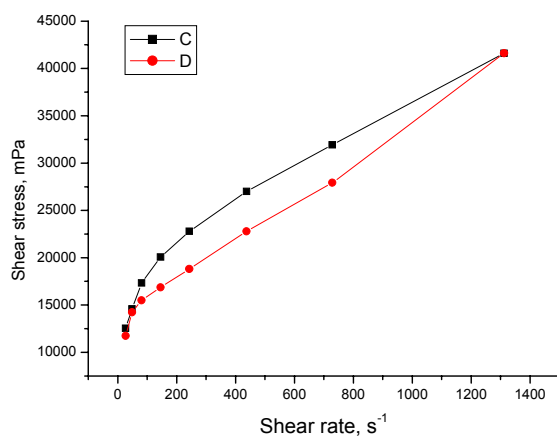


Fig. 1 – Rheograms of system a: C – increasing; D – decreasing of shear rates.

Introducing CMC into the above composition (a-CMC), the rheogram B from Figure 2 is obtained for the first increase of shear rates. It extends on a lower shear rate range compared with *a* due to the increase of viscosity produced by CMC, so its concentration is lower. But the value of viscosity at zero shear rate is lower, of 1238.39 mPa.s , on one hand due to the lower concentration of the system and on the other hand due to the higher shear rates on which the measurements were made ($27\text{-}1312$ and $48.5\text{-}1312\text{ s}^{-1}$, respectively).

The hysteresis loop, shown in the same Figure, is larger than that given by system a, which is a proof that it is more thixotropic, that is more sensitive to shear rate. Thus, it is not surprising that a second cycle increase-decrease of shear rates continue to decrease viscosity as the rheograms D and E in Figure 2 show, and a hysteresis loop also results. Continuing the cycle increasing-decreasing

remains constant at higher shear rates. The viscosity at zero shear rate obtained from the first part of the rheogram has the value 4600.87 mPa.s .

To establish if the intumescent composition a have time-dependent behaviour, rheological measurements were done also with decreasing shear rates (rheogram D, Fig. 1) and a hysteresis loop, that exhibits a thixotropic behaviour, resulted. This is demonstrated also by the viscosity at zero shear rate obtained using the data given by rheogram D, of 4256.49 mPa.s , about 8% lower than de previous one.

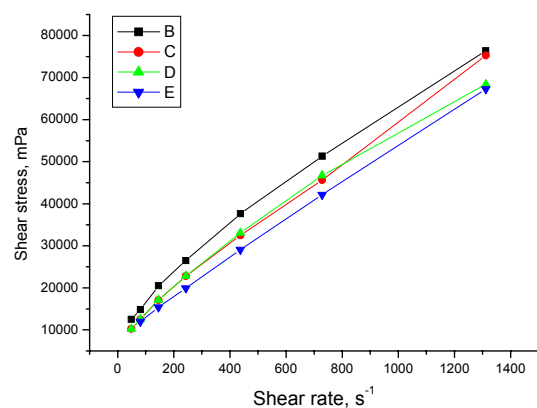


Fig. 2 – Rheograms of system a-CMC: B – increasing; C – decreasing; D – second increasing; E – second decreasing of shear rates.

of shear rates the rheogram E is reproduced, which demonstrates that the structure does not continue to modify.

Adding kaolin to the composition a – system 1a – the behaviour remains pseudoplastic (Figure 3), but the viscosity at zero shear rate increases 1.38 times, having the value 6349.94 mPa.s . This can be assigned both to its higher concentration and presence of kaolin, which acts as a thickener. Decreasing of shear rates results in rheogram D from the same Figure, placed under the rheogram C for shear rates higher than 437.4 s^{-1} and above it for lower ones, a proof that the system regain and even consolidates its structure at low shear rates. The value of viscosity at zero shear rate is much higher, of 9311.90 mPa.s , explained by the orientation of kaolin particles under the action of shear stress, which favours their interaction. Thus, this composition shows rheopexy at low shear rates and thixotropy at high ones.

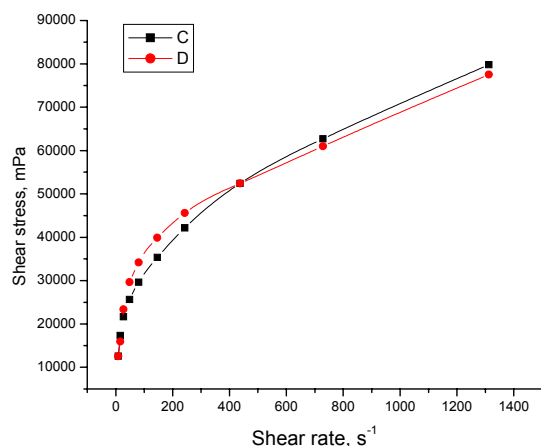


Fig. 3 – Rheograms of system 1a obtained with: C – increasing; D – decreasing of shear rates.

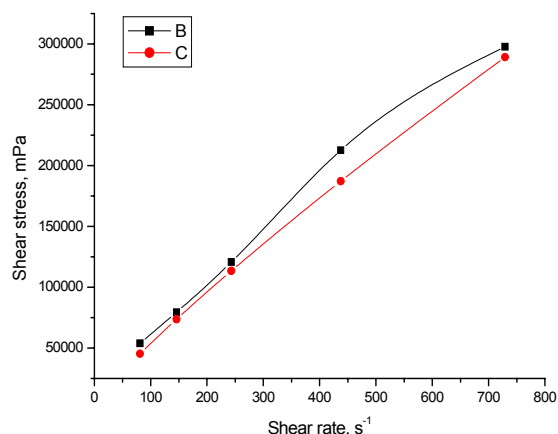


Fig. 4 – Rheograms of system 4a obtained with: B – increasing; C – decreasing of shear rates.

The rheological behaviour of the system 4b, which contains ammonium polyphosphate and sodium bentonite, is somewhat different: it shows ideal plastic fluid behaviour at low shear rates and pseudoplastic at higher ones for the first increasing of shear rates (curve B, Figure 4).

The linear part of the rheogram B results in a high value for the dynamic viscosity, of 15048 mPa.s, which is explained by the very high concentration of the system and higher dissociation of sodium bentonite compared with Luvogel 7, an organically modified calcium bentonite. When the shear rates are decreased, rheogram C was obtained, which shows an ideal plastic fluid behaviour. It is placed under the first one, which suggests that the composition is thixotropic.

The compositions spread well on metal and polyvinyl chloride surfaces, excepting b-CMC that gives a non-homogeneous film, as well as 1b and 3b, which are also difficult to spread, due to the presence of the insoluble compound ammonium polyphosphate.

The drying time must be long enough to eliminate the risk of curing during application and low enough to make possible the application of a second layer in due time. Being temperature and humidity dependent, 8 h were established for a temperature of 15-20°C, a relative humidity of 65% and a wet film thickness of 400 μm . The time between applications of successive layers is 24 h for such coatings. All the compositions in Table 1 correspond, having the drying times lower than 4 h (3.5 ± 0.25 h).

The best aspect of the wet film was obtained for 1b-CMC, followed by a, a-CMC, 1a, b, 2a and 4b, while b-CMC and 1b give non-homogeneous films and 3b spreads difficult, as column 4 of Table 1 shows.

The dry films have good aspect, excepting the compositions b-CMC, 1b and 3b that give also non-homogeneous wet films and have exfoliating tendency, due to their low adherence to the metal support.

The lowest value for adherence to metal was obtained for b-CMC, which gives also non-continuous wet film that becomes friable on drying. But even for this system the adherence is at the middle of the grid adherence scale. Somewhat lower grid adherences were obtained for compositions 1b and 3b that show also exfoliating tendency of films in dry state, property that can be assigned both to the ammonium polyphosphate and to the mineral fillers.

To select the most performing intumescent compositions, expansion of dry films deposited on low alloy steel OL 37 in laboratory conditions using an alcohol lamp was carried out. The values of the expanding indices were calculated as averages, excluding the maximum and minimum ones, and are given in the column 8 of Table 1.

Good fire protection can be obtained only for intumescent composition having expanding indices higher than 500% and very good for those exceeding 1000%. [1]

The data in Table 1 show that all the prepared compositions containing ammonium phosphate, a water-soluble acid donor that enters the intumescence process at a lower temperature compared with ammonium polyphosphate, can be classified as very good or good fire protecting coating, while those containing ammonium polyphosphate, a water-insoluble acid donor, as good or medium ones.

The highest value of expanding index was obtained for the composition a-CMC that combines the positive effects of ammonium phosphate and

CMC on char formation, the polymer acting not only as an anti-settling agent for dispersions, but also as a binder that controls the char expansion [9,25]. It is followed – in decreasing order of expanding indices – by 2a, 1a and a.

Carboxymethylcellulose has as effect the increasing of expanding indices irrespective of composition, due to the property the organic polymers has to control the char expansion [9].

The highest value of the expanding index for mineral charges was obtained for sodium bentonite (compositions 4b compared with b), followed by the organically modified calcium bentonite Luvogel 7 (3b compared with b), tri-hydrated alumina (2a and a) and kaolin (1a and a and 1b and b, respectively). Combined with CMC, the effect of kaolin is a little bit higher (1b-CMC and b-CMC).

Considering all the characteristics presented in Table 1, the most convenient intumescent system is a-CMC that contains ammonium phosphate and carboxymethylcellulose, followed, in decreasing order of expanding indices, wet and dry film properties and easiness of application by brushing by 2a, 1a, a and 1b-CMC. This conclusion will be verified using large samples and high heating powers. The composition 1a has also the highest passivating effect.

CONCLUSIONS

Aqueous ecological intumescent fire retardant coatings for multifunctional applications based on commercial sodium phosphate or polyphosphate, pentaerythritol and melamine as basic elements for char formation and titanium dioxide as pigment were obtained.

Ammonium phosphate as acid source gives more performing intumescent coatings both in the absence and presence of CMC and mineral charges.

Carboxymethylcellulose improves the properties of intumescent coatings, excepting the b-CMC system for which the wet film is non-homogeneous, the dry one is friable, the grid adherence has the lowest value and the char has open pores and is friable, so the expanding index is 1.36 times higher than that of the system that does not contain CMC.

Kaolin improves slightly the properties of ammonium phosphate-based coatings but reduces all the properties of that containing polyphosphate, excepting the expanding index, which is a little bit increased.

Tri-hydrated alumina has a positive effect on all the properties of the intumescent coating containing ammonium phosphate.

Organically modified calcium bentonite increases 1.28 times the expanding index but worsens all the other properties of polyphosphate-based coating.

Sodium bentonite improves all the properties of the polyphosphate-based coating.

The most convenient intumescent coating is a-CMC that contains ammonium phosphate and carboxymethylcellulose.

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