

Объединение независимых экспертов в области минеральных ресурсов,
металлургии и химической промышленности



Polyacrylamide (PAA) Production, Market and Forecast in Russia

Sample PDF

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Annotation

The present report is devoted to the market of polyacrylamide in the Russian Federation.

The research objective is the analysis of the Russian market of polyacrylamide.

The research object is polyacrylamide.

The presented work is **desk research**. **Information sources** were databases of Federal State Statistics Service of the Russian Federation (FSGS RF, Rosstat), customs statistics, statistics of rail transportation of the Russian Federation, the industry and regional press, the annual and quarterly reports of issuers of securities, websites of the enterprises of producers and consumers, and also the database of Infomine.

Chronological framework of research: 2007- 2015; the forecast – up to 2030.

Geography of research: Russian Federation – a complex detailed analysis of the market.

The report consists of **6** parts, contains **90** pages, includes **33** Tables, **20** Figures and the Appendix.

The first chapter considers the technologies of producing polyacrylamide and the raw materials used.

The second chapter is devoted to the analysis of production of polyacrylamide in Russia in 2007-2014. This section gives data on the quality of the product, which is released in the country, on volumes and the structure of its production, tracks the dynamics of productions by enterprises, considers the current status of its manufacturers (the outputs, plans for development of the enterprises, and also data on volumes and the directions of supplies of products in recent years). Projects of creation of new productions of polyacrylamide in Russia are also presented.

The **third** chapter of the report discusses the foreign trade operations with polyacrylamide in the Russian Federation from 2007 to 2015. Volumes and the directions of deliveries, the brand structure of the imported products are analyzed. The largest foreign companies-suppliers of polyacrylamide to the Russian consumers are presented.

The **fourth** chapter contains the analysis of the internal and export-import prices of polyacrylamide on the Russian market in 2007-2015.

The **fifth** chapter describes the market of the polyacrylamide consumption in Russia in 2007-2015. It analyzes in detail the dynamics and structure of consumption, and the production-consumption balance. The review gives the current status and perspectives of development of the main consuming industries.

The **sixth** chapter of the report provides the forecast of development of the Russian polyacrylamide market for the period up to 2030.

The Appendix gives addresses and contact information of the main Russian enterprises manufacturing polyacrylamide.

Target audience of the research:

- participants of the market of polyacrylamide – producers, consumers, traders;
- potential investors.

The offered research pretends to be a reference tool for the marketing services and specialists making administrative decisions at the market of polyacrylamide.

Introduction

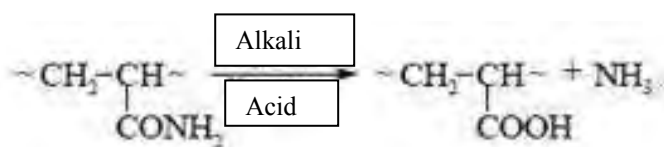
Polyacrylamide (PAA) is the general name of group polymers and copolymers on the basis of acrylamide and its derivatives. PAA is *polyelectrolyte*, that it is the polymer capable to dissociate to ions in water.

The PAA homopolymer – $(-CH_2CHCONH_2-)_n$ – is a solid amorphous white or a partially transparent flavorless substance; and with a molecular weight of 10^4 - 10^7 (depending on receiving conditions). Its density is 1.302 g/cm^3 (at 23°C); the glass-transition temperature, $T_{\text{glass.}} \sim 190^\circ\text{C}$. It dissolves in water, morpholine, formamide, glycerin, ethylene glycol, glacial acetic acid; it swells in propionic acid, dimethyl sulfoxide and propylene glycol; does not dissolve in alcohols, ketones, DMFA and non-polar solvents.

Properties of dry PAA do not change at a long-term storage, it is resistant to action of oils, fats, waxes. At temperatures higher than 60°C polyacrylamide starts destructing, which can lead to a loss of ability to dissolve in water.

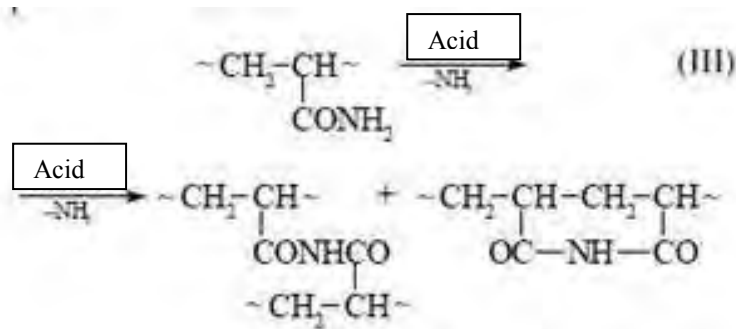
The PAA aqueous solutions are subject to action of microorganisms. The viscosity of aqueous solutions (of concentrations less than 15%) decreases at an increase of temperature and a shear rate, and under the influence of residual radical initiators as a result of destruction of basic chains of macromolecules. Solutions are stabilized by antioxidants (in the amount of 0.01-5 mass. %).

Reactions on amide groups are used for modifying polyacrylamide. So, at the alkaline hydrolysis at heating the amide groups (up to 70% of them) turn into the COONa groups, at the acid hydrolysis – into the COOH groups:



The alkaline hydrolysis is carried out under the influence of hydroxides and carbonates. A partial transformation of amide groups into carboxylated groups, and also the increases in the sizes of macromolecular globules and the viscosity due to the electrostatic repulsion of the same charges of the chain, result in amplifying the thickening, flocculating, structuring and other properties of polymers.

The acid hydrolysis is complicated by formation of insoluble products due to the reaction of imidization and the solubility loss:



Besides, PAA interacts with formaldehyde (a methylation reaction) in an alkaline medium (pH 8-10) at 20°C with formation of polymethylolacrylamide, which is applied to dressing of fabrics (an impregnation or a surface processing with a purpose of crease-proofing and rigidity), a dehydration of drain waters' precipitates and an enrichments of iron ores. The heating and acidification of the formed polymethylolacrylamide results in the chain-linking with formation of bridges (-CONHCH₂-O-CH₂NHCO-).

Reactions of linking of PAA are applied to receiving water-absorbing products, films, protective coatings and capsules for drugs, seeds, fertilizers. PAA can be linked at interaction with N, N'-methylene-bis-acrylamide.

The formation of three-dimensional structures is possible also at the action of acids on PAA, however the imide linkages collapse when pH increases to 10-12. PAA is also exposed to linkage at the action of formaldehyde in an acidic environment with formation of bridges (-CONH-CH₂-NHCO-). AA copolymers with unsaturated acids can be linked by ions of multivalent metals.

The processing PAA with formaldehyde and a secondary amine in an alkaline medium (the Mannich reaction) leads to an aminomethylated polymer, which by its flocculating ability surpasses an initial polymer. As this reaction is reversible, the Mannich base is stabilized by conversion into a salt form by means of neutralization with strong acids or alkylating agents (for example, alkyl halides, dimethyl sulfate, epihalohydrin). The result is a strong-base polycationite suitable for flocculation of negatively charged dispersions.

The Hoffman's reaction (an interaction of PAA with a large excess of alkali and a small excess of sodium hypochlorite) is used for receiving a weak-base polymer – polyvinylamine. A complication of this reaction is a destruction of macromolecules, which reduces the polymerization degree.

The reaction of sulfomethylation is necessary for receiving anion derivatives of PAA at its interaction with formaldehyde and sodium bisulfite in an alkaline medium (pH 13). Macromolecules along with sulfomethylated groups may contain carboxylated groups (owing to the alkaline hydrolysis of the amide groups), as well as unreacted amide groups. In this case effective soil-aggregating chemicals, antistatic agents for textile materials and flocculants for different types of suspensions are produced.

In general, the chemical reactivity of PAA with formation of different ionic derivatives, branched and linked products expands ranges of application of polymers.

Polyacrylamide and its copolymers belong to rather inexpensive polyelectrolytes with a unique complex of applied properties. They are effective flocculants, sizing additives, flotation agents, dispersants, thickening agents, agents of reduction of hydrodynamic resistance of liquids, soil formers, etc. (Table 1).

Table 1. Ranges of application and purpose of polymers of acrylamide

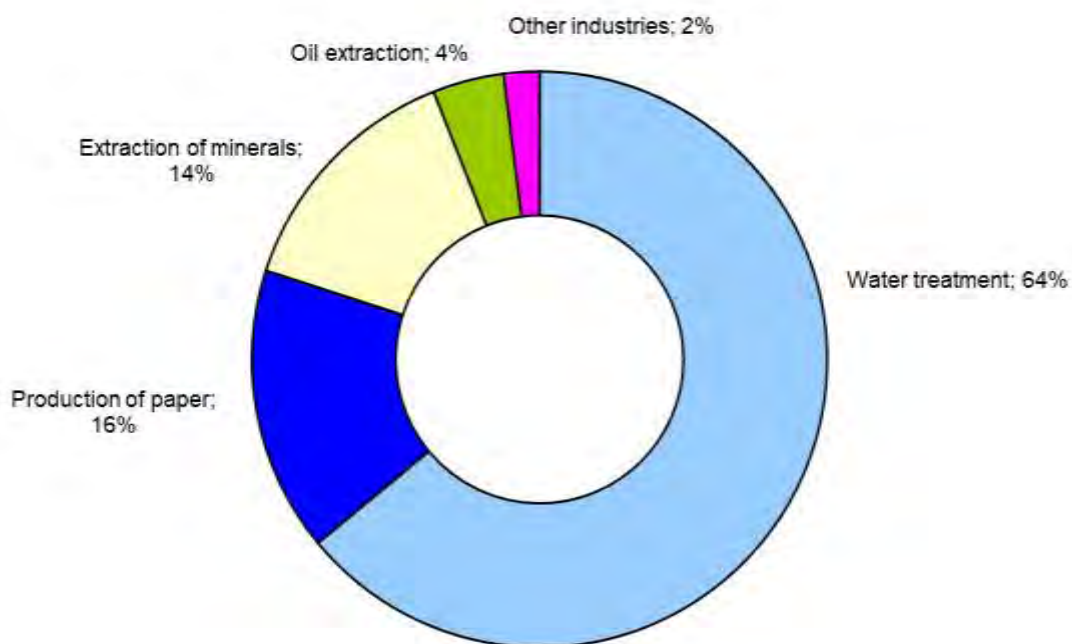
Application	Purpose
Water processing	Flocculants for purification of natural and industrial sewage, processing of foodstuff; the dehydrating agents for precipitates.
Paper processing	Paper strength regulators in dry and wet condition, additives to improve the quality and printing properties of paper.
Production and processing of minerals	Flocculants of tails of flotation of ores, at enrichment and regeneration of minerals (uranium, gold, titanium, black coal, aluminum, iron). Reduction of dust content in coal mines, when drilling, and at the asbestos plants.
Oil production	Stabilizers, regulators of filterability and rheological properties of drilling solutions. Soil formers for strengthening of walls of wells at a secondary oil production and hydraulic rupture of layers.
Agriculture	Soil formers. Filming agents for seeds, fertilizers, insecticides, herbicides and fungicides.
Medicine	Superabsorbent for tampons, pampers, napkins, diapers, bandages for wounds. Filming agents for pharmaceuticals of the prolonged action. Hydrogels for contact lenses.
Construction	Soil formers in road construction. Dehydrating agents for asbestos cement. Cement setting regulators. Strength additives for construction plates. Dispersants of pigments, regulators of viscosity and protective colloids for water emulsion paints.
Other areas	Agents reducing the hydraulic resistance for acceleration of movement of sea vessels, for pumping of oil products, suspensions and emulsions, for increase the long range of water jets in firefighting. Sizing agents for cotton, woolen, viscose and acetate rayon fibers. Dressing agents for fabrics. Glues for paper and textiles.

Source: review of specialized literature

Most often PAA are applied as *synthetic organic flocculants* for cleaning natural and drain waters (Figure 1). By abilities to the electrolytic dissociation such flocculants are divide into non-ionic and ionogenic.

Non-ionic flocculants are acrylamide homopolymers with the molecular weight from 5 to 15 million. The density of their charge is zero, i.e. they have neither positive, nor negative electric charge. Chemical modifying of PAA allows to produce non-ionic flocculants of various types and purpose.

Figure 1. Industry structure of world consumption of polyacrylamides in 2014, %



Source: FGBOU VPO Saratov State University named after N. G. Chernyshevsky

Ionogenic flocculants may be divided into anionic, cationic and ampholytic. The following anionic flocculants are applied in the industry:

- Partially hydrolyzed PAA containing in macromolecule 20-40% of carboxylate links;
- Products of the incomplete alkaline or acid hydrolysis of polyacrylonitrile with a various ratio of nitrile, amide and carboxylate groups;
- Homo- and copolymers of acrylic (AC) and methacrylic (MAC) acids.

Anionic flocculants with carboxyl (carboxylate) groups also include copolymers of maleic and fumaric acids. Of practical interest are flocculants with highly acidic groups (for example, sulfonate groups) on the basis of polystyrene, PAA, etc. polymers.

Cationic flocculants are especially effective when processing disperse systems with negatively charged particles. Weak-base cationic flocculants – polyvinylamine, polyethylene-imine, polyvinylpyridine and others, contain in their molecule primary, secondary and tertiary nitrogen atoms, strong-base cationic flocculants – polyelectrolytes with quarternary ammonium or pyridine groups (they are obtained by the exhaustive alkylation of nitrogen atoms of weak-base flocculants or by the polymerization of the corresponding monomeric compounds).

In particular, as cationic flocculants are used polymers of aminoalkyl ethers of acrylic (AC) and methacrylic (MAC) acids, vinylpyridines, diallylamine, diallyldimethylammonium chloride, alkylation products of polydimethyl-aminoethyl-methacrylate and polydiethyl-aminoethyl-methacrylate, products of sequential chloromethylation and amination of polystyrene or polyvinyltoluene, modified with

formaldehyde and secondary amine of PAA, containing in the macromolecule up to 30 mole % of cationic units.

Polyampholytic flocculants are usually products of copolymerization of acid (AC, MAC, maleic anhydride, etc.) and base (2-vinylpyridine, diallyldimethylammonium chloride, etc.) monomers. Among technological processes, for example, at flocculation of biological suspensions, polyampholytic flocculants have advantages before anionic and cationic.

The main use of non-ionic polymers is the cleaning natural and drain waters and dehydration of precipitates in the pulp and paper industry; the main use of anionic polymers is the water processing, flocculation of tails of flotation of ores, enrichment and regeneration of minerals and oil, processing of paper and dressing of textile materials (a creation on the surface of a thread of an elastic and strong film with a high water absorption capacity which anchors the acting fibers on the filament and improves the process of weaving and properties of the thread); the main use of cationic polymers is the processing of paper and flocculation of biological cells.

In the industry, polyacrylamide and also acrylamide copolymers (with methacrylic and acrylic acids, their salts and ethers, acrylonitrile, 2-methyl-5-vinylpyridine) are produced by the radical polymerization and the corresponding copolymerization of monomers.

A large-capacity production of polyacrylamide is carried out in 8-10% aqueous solutions under the action of oxidation-reduction systems, receiving the gel-like polyacrylamide with the molecular mass $(3-5) \cdot 10^6$, which, nevertheless, is difficult to transport, store and process. Concentrated aqueous solutions ($\geq 20\%$), inverse emulsions and suspensions are used to obtain polyacrylamide with the molecular weight $\sim 10^7$ under the influence of chemical initiators or the ionizing radiation.

The most widely applied acrylamide copolymer with salts of acrylic acid is produced, in addition, by polymerization of acrylamide in the presence of alkaline agents and by the alkaline hydrolysis of polyacrylamide in the inverse emulsions and suspensions.

The industrial production of polyacrylamide reagents has begun in the early fifties, and now the world production reaches 1.5 million tons a year and continues to increase steadily. Main suppliers of polymers on the world market are large companies of USA, Japan and the developed countries of Europe. Such countries as Russia, China, and the Republic of South Africa release polymers for their internal consumption.

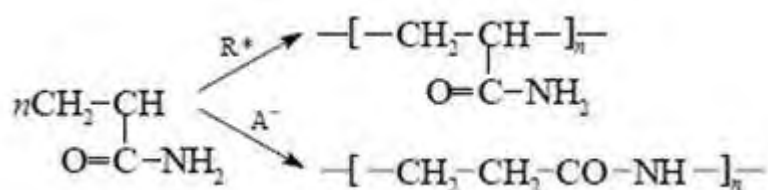
Polyacrylamide reagents are produced in the form of solutions, dispersions, granules or powder with a broad range of properties; depending on appointment they can be soluble, insoluble and swelling rubber-like gels.

I. Polyacrylamide production technology and the raw materials used in the industry

I.1. Methods of production of polyacrylamide

So, the term "polyacrylamide" (PAA) combines the whole group of polymers and copolymers on the basis of acrylamide and its derivatives.

Generally, polyacrylamide is received by polymerization of acrylamide (AA) under the influence of radical or ionic initiators, the ultra-violet or radiation, an ultrasound or the electric current. With simplifications, the radical and ionic polymerization can be presented by the scheme:



where R* and A are, respectively, a radical and an anion.

The radical polymerization is the main industrial method of receiving water-soluble PAA. Polymers of the greatest practical interest have a high molecular weight (10^6 - 10^7). For their production high purity monomers, small concentrations of the initiator, a lack of oxygen and impurity of ions of metals are required.

The polymerization of AA is significantly influenced by pH of a reaction medium. At low pH and high temperatures a formation of insoluble in water linked polymers is possible due to formation between macromolecules of imide linkages (-CO-NH-CO-), and at high pH the hydrolysis of amide groups takes place. The last reaction can be used for receiving during the polymerization stage of partially hydrolyzed PAA (up to 30%).

A polymerization can be carried out practically by all known methods: in solutions, emulsions, suspensions, and also in the mass of the crystalline or melted polymers. Depending on the way of polymerization, polymers can be obtained as solutions, granules, powders and dispersions in organic liquids.

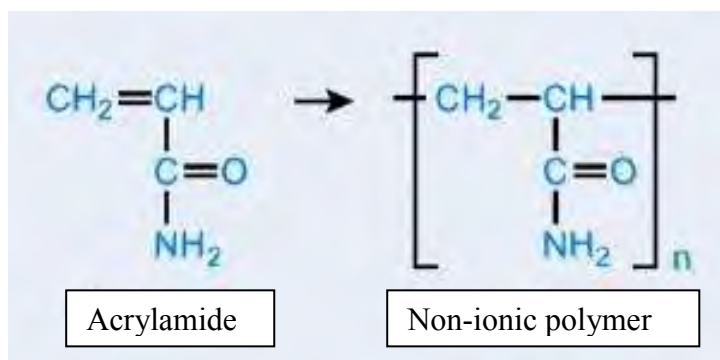
For polyacrylamide the number of solvents is small: water, acetic and formic acids. The widespread industrial method of receiving PAA is the polymerization of 4-9% aqueous solutions of AA in the oxidation-reduction environment in the presence of potassium persulfate, trietanolamine and sodium hydrosulfate.

The universal use of the polymerization in aqueous solutions is caused by a high reaction speed and the possibility of receiving polymers with molecular weights, unattainable at polymerization in organic solvents.

An initiation of the AA polymerization in redox systems has received the greatest use among others possible ways, as it allows to carry out the synthesis at rather low temperatures and does not require a complicated hardware setup.

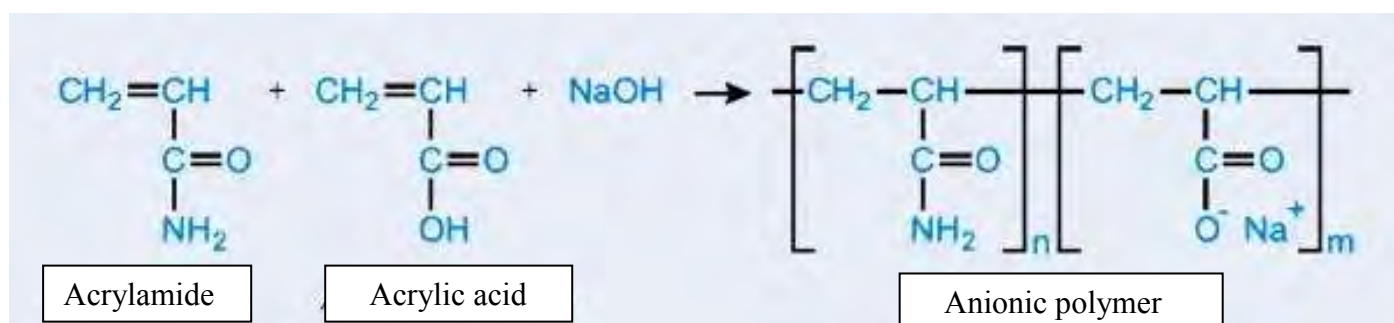
So far a large number of redox systems is offered. The most widely applied systems contain peroxides, bromates, chlorates, permanganates as oxidants, and compounds of two - and tetravalent sulfur as reducers. There are also numerous systems containing the salts of metals of a variable valence capable acting as either oxidants or reducers depending on their oxidation level. Salts of iron (II) are especially often used for an initiation of polymerization.

Non-ionic PAA are obtained by polymerization of non-ionic monomers of acrylamide:

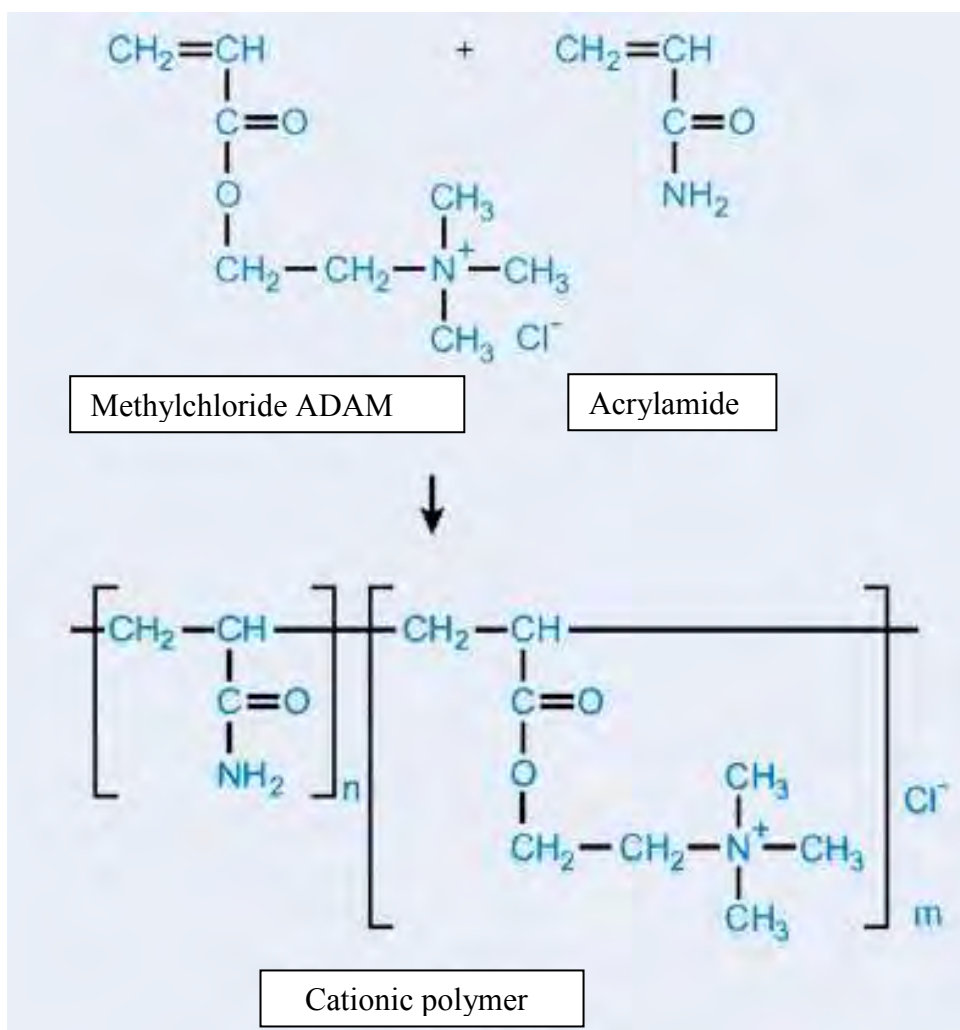


The radical copolymerization of AA with vinyl monomers is used for receiving copolymers which have better consumer properties in comparison with PAA. Non-ionic copolymers are produced by a copolymerization of AA with acrylonitrile, acrylates, and vinylidene chloride.

Anionic PAA are obtained by a copolymerization of acrylamide and a salt of carboxylic or sulfonic acids. More often acrylic acid is used:



Cationic PAA are obtained by polymerization of salts of the quarternary ammonium or the tertiary amine base dimethylaminoethyl-methacrylate (acrylate) or their copolymerization with acrylamide:



The graft and block copolymerization are used for modification of properties of polymers. Unlike usual copolymers, which links in chains chaotically or regularly alternate, chains of graft and block copolymers are constructed of the long sequences of links of one type. Graft copolymers have chains of a branched structure, and block copolymers – of a linear structure. With the use of radical initiators, ultra-violet and radiation exposure, AA is grafted on different polymers (for example polyolefins), and styrene, acrylonitrile, etc. monomers are grafted on PAA. Block copolymers are also obtained by the condensation of functional groups of different polymers, one of which is PAA.

The selection of the hardware and technological methods of production depends on the ways of the synthesis of acrylic copolymers.

The polymerization of acrylamide in diluted aqueous solutions is carried out in the reactor representing a capacitive apparatus with a jacket and a stirrer. The polymerization began at 20-25°C. In the course of reaction the temperature reaches 35-45°C. After the end of synthesis the reaction mass is squeezed out from the reactor.

The periodic method of production in solvents has essential shortcomings: many stages of processes, and a large number of manual operations. The most

economic method is the process of receiving polymers in the concentrated aqueous solution with a continuous scheme at almost a total absence of waste.

It should be noted that production of a polymer of acrylamide demands a strict observance of technologies. It is caused by the fact that acrylamide is toxic, fire-dangerous and explosive.

The homogeneous polymerization of AA in aqueous solutions historically was the first, simplest and pollution-free method of receiving polyacrylamide.

Usually polymers, synthesized by this method, are obtained in the form of gels of different concentrations (most often 7-11%). In case of need, the dry polymer may be separated by a sedimentation with organic solvents, by drying the crushed gel or by an azeotropic distillation of water with organic solvents. In most cases, the stage of the polymer separation is absent, and polyacrylamide gels are used as marketable products.

The granulated polyacrylamide with the content of the main substance 82-98% is more convenient for transportation and use.

I.2. Raw materials for production of polyacrylamide

The main raw materials for obtaining polyacrylamide is acrylamide, which is received, in turn, by:

1. The hydrolysis of acrylonitrile (acrylic acid amide) with 84.5% H₂SO₄ at 80-100°C in the presence of inhibitors of polymerization (salts of Cu or Fe, sulfur, phenothiazine, etc.). The formed sulfate salt of acrylamide is neutralized by the stoichiometric amount of NH₃ or lime milk.

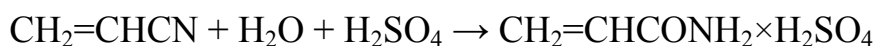
2. The catalytic hydrolysis of acrylonitrile at 80-120°C in the presence of copper catalysts (Rene's copper, Cu/Cr₂O₃, Cu/Al₂O₃-SiO₂, etc.). The yield of acrylonitrile is 98.5%. The main impurity is β-hydroxypropane nitrile (up to 0.1%). This way of production is more preferable than the sulfuric acid method in economic and ecological terms.

As it was already noted, acrylamide is fire hazardous, explosive, and toxic. It strikes, mainly, the nervous system, and also liver and kidneys; easily gets through an undamaged skin; irritates mucous membranes of eyes; LD₅₀ is 150-180 mg/kg (rats, pigs, rabbits; orally); MPC is 0.3 mg/m³.

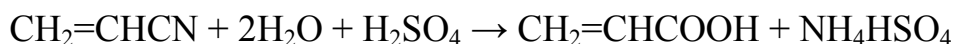
For the first time acrylamide has been received in 1893, however the development of its industrial production has begun only in the beginning of the 50th years of the XX century because of the insufficient source of raw materials (a complexity of receiving acrylonitrile).

In 1954, American Cyanamid Company (USA) implemented on the commercial scale the method of the sulfuric acid hydrolysis of acrylonitrile with the subsequent neutralization of hydrogen chloride or acrylamide sulfate by caustic potash or aqueous solution of alkali.

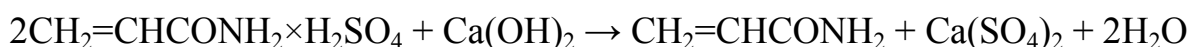
In the Soviet Union, the industrial way of receiving crystal acrylamide was mastered in 1961. By this way acrylonitrile is saponified by monohydrate of 80-85% sulfuric acid at 358-373 K:



This reaction usually proceeds with the formation of small amount of acrylic acid (up to 4%):



At the following stage, the neutralization of acrylamide sulfate with calcium hydroxide takes place and the release of acrylamide in its free state in the form of an aqueous solution:



Acrylamide sulfate, received at the acrylonitrile saponification, is neutralized in an aqueous medium with Ca(OH)₂, ammonia, sodium carbonate or potassium carbonate, and also with compounds of alkali or alkaline earth metals with addition of

water or an organic solvent. The suspension after neutralization is filtered with receiving the solution of a monomer and the corresponding salts of sulfuric acid.

In the course of receiving acrylamide by the hydrolysis of acrylonitrile in the presence of sulfuric acid inhibitors are applied to prevent the polymerization of a monomer, for example, nitrobenzene, nitro-*o*-cresol, biphenyl amine, diethyl amine, dicyanhydroquinone.

The sulfuric acid hydrolysis of acrylonitrile to acrylamide was successfully applied in the industry until 1970. Now the most promising method is the production of acrylamide by the catalytic hydration of acrylonitrile into acrylamide in the presence of the solid catalyst – metallic copper.

The copper catalyst can be received by the copper dusting in an organic solvent or by the reduction of the inner-complex compound of copper applied on aluminum oxide or active coal.

The result of the catalytic hydration is 10% aqueous solutions of acrylamide. However, for polymerization more concentrated solutions 30-50% (mass.) acrylamide are applied. Concentrated solutions are obtained by the water evaporation in contact with air: oxygen is an inhibitor of polymerization.

In the Russian Federation acrylonitrile is produced only by OOO Saratovorgsintez (Lukoil company) which delivers this product practically to all producers of polyacrylamide.

II. Production polyacrylamide in Russia in 2007-2014

II.1. Quality of polyacrylamide produced in the Russian Federation

It should be noted that in the USSR polyacrylamides were released in compliance with TU 6-01-1049-92 (ammoniac) (Table 2).

Table 2. Physical and chemical indicators of polyacrylamide-gel technical of the ammoniac brands on TU 6-01-1049-92

Indicator	Standard		
	Prime grade	1 grade	2 grade
Mass fraction of the main substance, %, at least	6.0	6.0	5.0
Kinematic viscosity of polyacrylamide-gel solution with mass fraction of 0.25% in sodium chloride solution with mass fraction of 3% at 30°C, mm ² /sec, at least	4.6	3.0	2.2
Deposition rate on copper oxide, mm/sec, at least	12.0	8.0	4.0
Mass fraction of residual monomers per 1% of the main substance, % acrylamide, at most	0.005-0.025	0.005-0.025	0.005-0.025
Sum of unsaturated compounds, at most			

Source: TU 6-01-1049-92

In the middle of the 2000th, TU 6-01-1049-92 was changed with technical regulation TU 2414-002-74301823-2007, developed and introduced by OAO Poliflok. According to this TU, the flocculant is made in the following forms: non-ionic, anionic, aqueous solution, granulated.

Designations: Poliflok X-YY-ZZ(W), where:

X – a type of ionic activity: A – anionic, N – non-ionic;

YY (05-25) – molecular weight (million units);

ZZ (00-90) – a degree of hydrolysis;

W (6-8) – a mass fraction of the main substance in an aqueous solution (% weight).

An example of the product identification number:

1. POLIFLOK N-0605 (6) TU 2414-002-74301823-2007 is a 6% solution of non-ionic flocculant, the molecular weight is 6 million units, the degree of hydrolysis is 5%.

2. POLIFLOK A-1515 TU 2414-002-74301823-2007 is an anionic flocculant in a dry form, the molecular weight is 15 million units, and the degree of hydrolysis is 15%.

An aqueous solution Poliflok R represents the colorless or yellowish color gel-like viscous mass. It is obtained by polymerization of a solution of acrylamide, synthesized on the biocatalyst with the use of oxidation-reduction initiators.

The granulated Poliflok S represents a water-soluble powder of a white color with a particle size no more than 1.4 mm, the density of 1150-1200 kg/m³, with a bulk weight of 600-800 kg/m³. It is received from the polyacrylamide solution by means of drying with the subsequent crushing.