Research Group

InfoMine

Association of Independent Consultants and Experts
in the Field of Mineral Resources, Metallurgy and Chemical Industry

Carboxymethylcellulose Market Review Over CIS

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SUMMARY

Carboxymethylcellulose (CMC), chemical composition of which is $[C_6H_7O_2(OH)_{3-x}(OCH_2COOH)_x]_n$, is a product of interaction between cellulose and monochloroacetic acid. Production of CMC, as well as its sodium salt, is carried out at some specialized enterprises located over the territory of Russia, Ukraine, Byelorussia and Uzbekistan, the total production capacity of them being on the level of 60 kt per year.

In 2005, production of carboxymethylcellulose was about 13.5 kt in CIS, which is practically equal to the corresponding index of the previous year, exceeding it less than by 3%. At that, over 85% of the total volume of CMC produced in the Commonwealth was produced at Russian industrial enterprises, their total production volume being 12.0 kt of the output (that is about a third part of the total potential of Russian Federation).

As to pattern of foreign-trade transactions, import volume of carboxymethylcellulose in RF has several folds exceeded that of export. In 2005, domestic companies delivered for abroad 1.08 kt of CMC, which 1.3 fold exceeded the corresponding index of the previous year. At that, in 2005, four manufacturers exported the product, as well as some trading companies, the share of which in the pattern of foreign deliveries was 15.6%. Volume of carboxymethylcellulose imported in Russia reached 7.55 kt, which is 2.4% more than the index of 2004.

Realization of different brands CMC by domestic manufacturers was carried out in 2006 at prices within the range of 33-70 rubles/kg (adjusted for VAT). Average export price was $1.77 per kg in 2005, which exceeded the index of the previous year by 13.5%; import price was $1.36 per kg (18.3% more as compared with that of 2004).

In 2005, “apparent” consumption of carboxymethylcellulose maintained on the level of the previous year, i. e. 18.5 kt. The major part of the product was used at enterprises of gas and oil industry, which purchased 5.3 kt of CMC, i. e. 28.6% of the total all-Russian consumption. Besides, carboxymethylcellulose was widely used at production of building materials and synthetic detergents. In those segments of Russian economy 3.8 kt and 2.0 kt of the product was consumed, respectively.

Analyzing the dynamics of production, as well as of foreign-trade transactions with CMC in the recent years, allowed the experts of “InfoMine” forecasting further expanding of the market of the product in CIS for medium-term prospects. According to our forecast, consumption of carboxymethylcellulose will increase up to 26 kt by 2010, which will comprise about 40% of the total potential for CMC production in CIS, which will be reached by that moment.

INTRODUCTION

Carboxymethylcellulose (CMC), also called tylose, "valotsel", "blanose" and "edifas", is, in general, a product of interaction between cellulose and monochloroacetic acid, described by a chemical formula such as $[C_6H_7O_2(OH)_{3-x}(OCH_2COOH)_x]_n$. This chemical combination is an amorphous colorless substance possessing properties of weak acid.

Sodium salt of carboxymethylcellulose is of the most practical importance, which salt is, like CMC, an amorphous colorless substance with density of 1.59 g/cm^3, whereas its bulk density is 300-800 kg/m^3. Possessing softening temperature of 170°C, the sodium salt of CMC is soluble in water, as well as in water solutions of alkali, ammonia and sodium chloride, solubility degree depending on the degree of etherification of cellulose. On the contrary, the product is not soluble in organic solvents and mineral oil.

At solution in water, sodium salt of carboxymethylcellulose forms viscous clear solutions characterized by apparent viscosity, and some sorts are also characterized by thixotropy (i. e. ability of spontaneous recovering original structure broken by mechanical force). In water solutions, the sodium salt of CMC, performing properties of a surface-active substance (SAS), readily combines with other water-soluble cellulose ethers, natural and synthetic polymers, as well as with many salts of alkali, alkali-earth metals, and ammonium. The combination is destroyed in water solutions of mineral acids and alkali exposed to oxygen. Water solutions of the sodium salt of CMC form transparent films characterized by percent elongation of 8-15%. Being processed by bi- and poly-functional combinations, the films become insoluble.

Under the action of salts of polyvalent and heavy metals, a corresponding salt of CMC, insoluble in water, is precipitated, and under the action of mineral acids, carboxymethylcellulose itself.

Dry sodium salt of CMC has a small corrosive effect, is not biologically active, and is resistant to biological degradation; however, its water solutions are subject to enzymatic hydrolysis when exposed to air too long. For such solutions, benzoic and sorbic acids and their salts, chlorinated phenols, formaldehyde or iodine, are used as preservative agents.

Sodium salt of carboxymethylcellulose is widely used in industry. The combination is used as stiffener and stabilizer for clay suspensions at boring oil and gas holes, as flotation agent at dressing of copper-nickel and potassium ores, as re-sorbent of soil in synthetic detergents, as sizing agent for thread of base, stiffener for printing ink, component of mixtures providing plasticity of ceramic mass and regulating rheological properties of cement suspensions.

The product containing over 95% of the sodium salt of CMC is used as stiffener and softener for coating mixtures of welding electrodes, stiffener for tooth-pastes, makeup preparations and foodstuff (in particular, juices and mousses).

I. Technology of Production of Carboxymethylcellulose and Raw Materials Used in Industry

I.1 Methods of Production of Carboxymethylcellulose

The main industrial method of production of carboxymethylcellulose is that of interaction between alkali cellulose and monochloroacetic acid (or its sodium salt) at the presence of caustic soda [NaOH], ratio between reactivity of OH groups in elementary units of cellulose is 2.14:1:1.58 among C-2, C-3 and C-6 atoms.

At present, two schemes of technological process for industrial producing carboxymethylcellulose have become widely used, namely ***periodical*** (classic) and ***mono-unit*** ones. At that, the technology of production of CMC usually involves several stages, at first of which alkali cellulose is produced when processing its wood or cotton sorts with water solution of caustic at the presence of organic solvents, as the latter lower alcohols are usually used (in rare cases, the process is carried out without any solvents). Further, interaction is realized between the alkali cellulose and monochloroacetic acid at a temperature of 80-100°C in case of using solvents (and at 70-80°C without solvents) with further drying, grinding and packing the product.

One of the principal conditions for obtaining high-quality products is providing conditions, which exclude mashing and squeezing of the cellulose fiber, leading to lowering (and, in some cases, to a zero speed) penetration of the chemical agents to it at the process of carbonic methylation.

In general, technical product contains about 50-70% of ether (it is washed with water solutions of lower alcohols to obtain more pure carboxymethylcellulose). To raise the quality of commodity product, experts of Kazan State Technological University have developed a new technology for obtaining purified sodium salt of CMC. The first variant of its realization supposes two-stage washing of the product with alcohol-water solution, on the first stage, 50% alcohol solution being used, which is supplied from the second stage of washing (on the second stage, 94-96% alcohol solution is used). At that, thorough expression after each washing is of great importance (up to 50-70% residual moisture). The degree of such purification reaches 98.5% of base material.

According to the second variant of realization of the technology of producing purified sodium salt of carboxymethylcellulose, developed by experts from Kazan, the process supposes inversion purifying of the technical product. On the first stage of this process, sodium salt of CMC is transformed into acid form by processing it with 20% sulfuric acid. Further, this combination, characterized by insolubility in water, is repeatedly washed with water for eliminating the major part of impurities.

On the final stage of the process, the acid form is once more transformed into sodium salt of CMC (by processing with 4% solution of caustic soda in alcohol), which is further washed with alcohol. The degree of purification of such obtained product is not less than 99% of base material, on condition that softened water is used for washing. Dosing supply of alcohol is about 5-6 g/t of purified sodium salt of