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POLYCARBOXYLATE CEMENT GRINDING ACCELERATORS BASED ON RECYCLED RAW MATERIALS AND MANUFACTURING WASTE

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ABSTRACT

Introduction. This article focuses on the development and physicochemical investigation of new composite cement grinding accelerators based on recycled nitron fibers (from old carpet products) and waste products from oil and coke refining. The objective of this study is to develop and conduct a comprehensive physicochemical investigation of the structure of new composite cement grinding intensifiers based on the products of alkaline hydrolysis of domestic polyacrylonitrile raw materials and aliphatic amino alcohols (methyl diethanolamine and triethanolamine). **Materials and Methods.** Water-soluble polycarboxylate esters were synthesized as the polymer matrix via controlled alkaline hydrolysis of polyacrylonitrile (PAN) fiber waste, followed by acid esterification with methanol. The resulting polymer matrix (yield: 31.2 g) was combined with secondary amino alcohols derived from oil and gas refining-methyldiethanolamine (MDEA) and triethanolamine (TEA)-in a mass ratio of 1:9. **Results and Discussion.** The extent of the chemical transformations was rigorously confirmed by Fourier-transform infrared spectroscopy: complete opening of the triple bonds of the PAN nitrile groups (2243 cm^{-1}) and the formation of characteristic bands of carboxylate anions (1573 and 1404 cm^{-1}), as well as amide and ether groups. Chromatography-mass spectrometry data confirmed the high purity of the target products. **Conclusions.** From the perspective of physicochemical mechanics (the Rebinder effect), the mechanism for intensifying clinker grinding was theoretically substantiated. It has been shown that the system with TEA provides the maximum steric barrier, while the system with MDEAs facilitates accelerated diffusion into microcracks, which prevents re-agglomeration and improves the efficiency of cement grinding.

KEYWORDS: cement grinding accelerators; polyacrylonitrile; methyldiethanolamine; triethanolamine; cement clinker.

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1 INTRODUCTION

Currently, introducing energy-saving, economic, and ecological technologies in the construction industry is a strategically important task. The efficiency of cement production largely depends on the quality of clinker grinding, which requires significant energy and resource inputs, making it a key strategy for improving the efficiency of this process. - the use of grinding accelerators, which not only increase the productivity of mills but also allow for the improvement of the main characteristics of the finished product.

Cement grinding accelerators are additives that significantly speed up the clinker grinding process in cement plants. Their use allows for reducing the energy intensity of production, increasing efficiency, and lowering costs. Currently, accelerators such as gypsum, plasticizers, or special chemical admixtures that interact with the cement, reduce its viscosity, and promote rapid grinding are used. This makes it possible to create an environmentally friendly and cost-effective cement production process. To a certain extent, accelerators are aids that facilitate difficult processes. Grinding accelerators are chemical additives designed to reduce energy consumption by decreasing the adhesion of the ground material to the equipment's working surfaces, ensuring efficient and uniform grinding. These additives increase the fineness of the cement and positively affect its final properties [1-3].

Modern research on the use of grinding accelerators is aimed at increasing the energy efficiency of cement production and improving product quality. For example, the use of additives such as coal or coke significantly increases grinding efficiency and positively affects cement strength. To achieve optimal cement properties, a comprehensive approach to the selection and use of additives and the optimal organization of every stage of the production process is required. Today, the selection of effective grinding activators and additives is a significant task that requires a well-thought-out strategy and a detailed analysis of all possible factors and their impact on the production process and product properties [4].

In modern cement production, open and closed mills are widely used, with closed mills being particularly common because they allow for high efficiency in the distribution of multi-component products. The process of dividing material into fractions enables achieving a uniform consistency and fineness of the grind. This prevents over-grinding and reduces energy consumption. Optimizing the grinding process begins with the proper selection of the initial material, which consists of various components with different grinding properties.

When accelerating cement grinding in ball mills using accelerators, they act on the material and alter the technological parameters and properties of the finished cement. A complete classification of the technological additives used in cement grinding is presented in [5]. According to that classification, the additives used are divided into grinding accelerators and additives that improve the cement's construction and operational properties.

Accelerators widely used in modern cement production to increase grinding efficiency [6, 7]:

- Gypsum accelerates the setting and hardening of cement clinker, increasing its activity.-Plasticizers and superplasticizers, which reduce the mixture's viscosity, help to decrease the energy consumption of the grinding process.

- Graphite additives, which reduce friction in the ball mill, increase grinding efficiency.-Silico-organic compounds increase the dispersion and activity of cement particles.

- Bi-components (e.g., ferrites and certain cations) activate the mineral components, accelerate grinding, and are used to improve cement quality.

Interestingly, the use of accelerators not only increases the mills' productivity but also reduces energy consumption, which is very important in modern production. The grinding accelerators introduced into the mill alter the surfaces of newly formed particles, prevent

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them from sticking together, and facilitate grinding. For example, it was determined that S-Drill™ Intensive increases the performance of processing equipment by 9% and reduces energy consumption by 10% by improving these characteristics [8]. The innovative component neutralizes electrical charges, thereby preventing their aggregation and improving the physical properties of the cement. Thus, the use of grinding intensifiers, such as S-Drill™ Intensive, is aimed at improving the grinding process, the high quality of cement products, and reducing energy consumption during the production process [8].

The most popular grinding accelerators on the market are triethanolamine (TEA), triisopropanolamine (TIPA), polyethylene glycol (PEG), and fatty acid salts such as calciumstearate [9–15]. The results show that certain grinding aids, especially TIPA, ensure the early development of the mechanical properties of cementitious materials, particularly early strength [15].

The authors show that using polycarboxylate ether (PCE) as a grinding-enhancing admixture is effective [16–19]. These studies have shown that PCE increases grinding efficiency by forming an adsorbed layer on cement particles, thereby reducing their agglomeration. PCEs are molecules composed of hydrophilic side chains derived from negatively charged backbones and polyethylene glycols. The molar ratio between the unsaturated carboxylic acid and the macro-monomer bearing the side chain, as well as the length of the side chain, can be easily varied and precisely selected for specific conditions [20, 21]. The authors investigated the optimal chemical composition and structure of methacrylate ether-based polycarboxylate superplasticizers as an auxiliary tool for grinding cement under laboratory conditions [21].

Lu Wei, Zhang Ming, and Chen Li [22, 23] investigated the possibility of using polycarboxylate ether as a chemical accelerator in the cement grinding process, and found that the polycarboxylate ethers adsorb onto the surface of cement particles, significantly reducing the cohesion between them, allowing the particles to grind independently without sticking to each other and increasing the grinding efficiency by approximately 18%. Furthermore, it was shown that polycarboxylate ethers increase the dispersity of the particles and promote their uniform distribution, thereby increasing the overall efficiency of the process. Zhao Ming and his colleagues also conducted an in-depth analysis of the potential of mechanical intensifiers in reducing inter-particle interaction forces and accelerating the grinding process. They demonstrated that high-frequency vibrations are capable of reducing inter-particle friction and increasing milling efficiency by 15–25% [23].

The authors of [24] investigated the effect of organic acids and surfactants, used as chemical accelerators, on the mechanical properties of cement particles. The study showed that organic acids reduce particle adhesion by chemically interacting with the particle surface, while surfactants ensure particle separation and uniform dispersion. As a result, the milling of the particles is accelerated, and the grinding process is significantly speeded up due to the reduction of friction between them.

The authors of [25] conducted an in-depth analysis of the mechanism of action of chemical accelerators, determining that they alter the surface free energy of cement particles and promote their fine and uniform dispersion. The change in surface free energy reduces interparticle cohesion, facilitating their pulverization. This mechanism is recognized as a key factor in enhancing grinding efficiency by reducing interparticle interactions.

A group of authors [26] investigated the combined use of chemical and mechanical activators and analyzed their effect on particle dispersion and the grinding speed of cement. The results showed that using both types of activators together increases grinding efficiency by approximately 30%. It was determined that while mechanical accelerators

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promote particle separation, chemical accelerators allow for more effective particle modificatio.

In 2022, Garcia Luis F, along with his colleagues, developed a new formula for chemical accelerators and experimentally tested its effect on the cement grinding process. They found that these accelerators chemically modify the particle surface, reduce the tendency of particles to stick to each other, and significantly accelerate the grinding process. The effectiveness of the accelerators is associated with the strong adsorption of the active components on the particle surface, which contributes to a further increase in its efficiency [27].

In ball mills, the technological additives that influence material grinding and the final properties of the product play a crucial role in the process of grinding cement clinker. However, conventional accelerators are produced using complex technologies and require expensive raw materials, which limits their widespread and cost-effective use. Therefore, the development of activators produced from local raw materials and using simple technology is a pressing issue of our time.

2 METHODS AND MATERIALS

The objective of this study is to develop and conduct a comprehensive physicochemical investigation of the structure of new composite cement grinding intensifiers based on the products of alkaline hydrolysis of domestically produced polyacrylonitrile feedstock and aliphatic amino alcohols (methyldiethanolamine and triethanolamine).
To achieve this objective, the following tasks were addressed in this work:

- the targeted synthesis of water-soluble sodium polyacrylate via the alkaline hydrolysis of PAN fibers in an aqueous-alcoholic medium, followed by the isolation of the target product;
- to develop formulations for complex grinding intensifiers based on a combination of hydrolyzed polyacrylonitrile (GIPAN) with MDE and TEA in specified ratios;
- confirmation of the structure and identification of functional groups in the synthesized additives using IR spectroscopy and chromatography-mass spectrometry;
- theoretical justification of the mechanisms of adsorption interaction between the developed compositions and the surface of cement clinker minerals.

Substandard fibers and secondary waste from polyacrylonitrile processing (recycled PAN fibers, “nitron”) were used as the main polymer feedstock for the synthesis of polycarboxylate cement grinding intensifiers.

An 8% aqueous solution of sodium hydroxide (NaOH, analytical grade) was used for the hydrolysis of nitrile groups. Methanol (CH_3OH, analytical grade) was used as the esterification agent, and hydrochloric acid (HCl, analytical grade) was used as the catalyst for the esterification and neutralization stages.
To create complex synergistic compositions, secondary amino alcohols-a byproduct of the Shymkent Oil Refinery containing fractions of methyldiethanolamine (MDEA) and triethanolamine (TEA)-were used.
Methodology for the synthesis of polycarboxylate esters and composite additives. The production of grinding intensifiers was carried out experimentally using specialized laboratory equipment and included the following sequential process steps:

Raw Material Preparation: Secondary waste consisting of substandard PAN fibers was mechanically ground to a homogeneous consistency and pre-cleaned to remove oil residues and surface contaminants.

1. Alkaline destruction and hydrolysis: The prepared PAN was treated with an 8% sodium hydroxide solution at elevated temperature and autoclave pressure. During this process, extensive hydrolysis of the nitrile groups (–C=N) to carboxylate and amide fragments occurred, accompanied by the opening of the PAN backbone and the transition of the polymer to a water-soluble state (sodium polyacrylate).

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2. Acid esterification: Methanol was added to the resulting hydrolysate in the presence of hydrochloric acid as a catalyst. Inthisprocess, polycarboxylic acid (or its salt) reacted with the alcohol to form polycarboxylate ester groups according to the following scheme:

$(–CH_2–CH(COONa)–)_n$ + ROH-HCl $(–CH_2–CH(COOR)–)_n$ + NaOH + [NaCl]

3. Isolation and Purification: The target polycarboxylate ester was precipitated from the reaction mixture by adding an excess of methanol (150 mL). The resulting precipitate was separated by filtration through a Buchner funnel under vacuum. The filter residue was successively washed with methanol until all traces of chloride ions (Cl-) in the mother liquor had completely disappeared (verified by AgNO3). The purified product was dried in air for 48 hours to constant weight. The yield of dry polymer was 31.2 g. The product is a white, water-soluble powder that melts with decomposition.

4. Preparation of Compositions: In the final stage, the purified hydrolyzed polycarboxylate ester was combined with secondary alkanolamines (MDE or TEA) in a specified mass ratio of 1:9 to obtain complex grinding intensifiers.

Analytical Methods. The chemical structure, purity, and functional composition of the starting materials and synthesized intensifiers were identified and determined using a suite of physicochemical methods:

Fourier-transform infrared spectroscopy (FTIR): Absorption spectra were recorded on a Fourier-transform spectrometer in the wavenumber range of 4000–500 cm^{-1} to identify characteristic bands of carboxylate (-COO-), ether (-COOR), and amino groups.

Chromatography-mass spectrometry (CMS): was used to evaluate the molecular weight distribution of the products, as well as to identify the composition of secondary amino alcohols and volatile fractions.

The physicochemical, technological, and structural-technical properties of the resulting cement grinding intensifiers were determined based on standard methods and GOST standards adopted in the cement industry.

3 RESULTS AND DISCUSSION

As noted above, the physicochemical analysis of the raw materials and the resulting intensifiers was conducted using IR spectroscopy, chromatography, and mass spectrometry, while the physicochemical and chemical properties of the synthesized intensifiers were determined using standard methods.

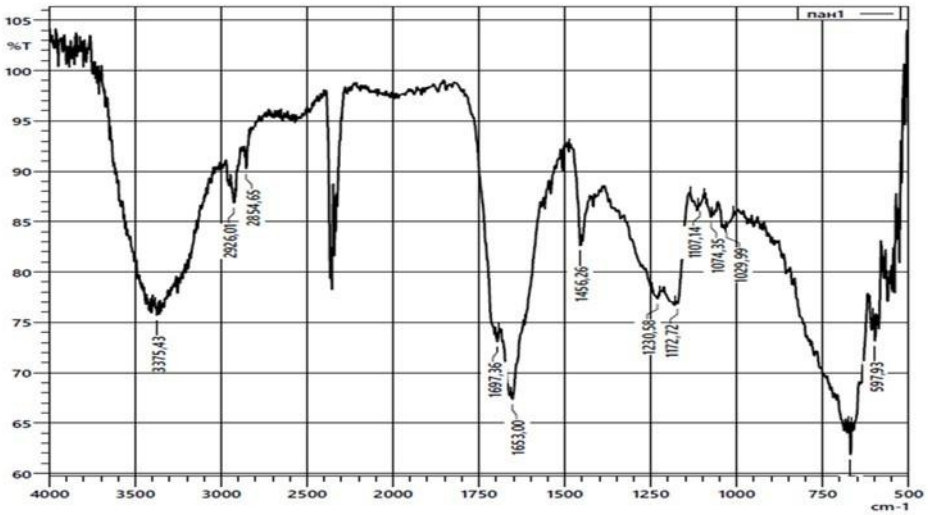


Fig. 1. IR spectra of hydrolyzed polyacrylonitrile (GIPAN)

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The chemical transformations that occur during the preparation of hydrolyzed polyacrylonitrile (GIPAN) are clearly confirmed by changes in its IR spectrum. In the high-frequency region, a strong, broad peak is observed with a maximum at 3309.85 cm^{-1}, attributable to the valence vibrations of the O–H bonds in associated water and hydroxyl groups, as well as the valence vibrations of the N–H bonds in unsubstituted amide fragments ($–CONH_2$), which formed at an intermediate stage of hydrolysis. Valent asymmetric and symmetric vibrations of the C–H bonds in the main polymer chain ($–CH_2–$, –CH–) are observed at 2945.30 and 2881.65 cm^{-1}; their shift relative to the initial PAN indicates a change in the conformation and chemical environment of the macromolecular chain. The nearly complete disappearance of the characteristic peak of the nitrile groups (–C≡N) in the region of ~2243 cm^{-1} indicates a high degree of conversion of the starting material.

The successful completion of the saponification process is confirmed by the appearance of the Amide I band at 1668.43 cm^{-1}, which corresponds to the valence vibrations of the C=O carbonyl groups in the amide linkages. Key markers of the target structure of GIPAN are the intense bands at 1573.91 and 1406.11 cm^{-1}, which correspond to the asymmetric and symmetric valence vibrations of the carboxylate ion ($-COO^-$). The presence of this conjugated doublet provides strong evidence for the formation of sodium polyacrylate salt fragments. The band corresponding to the in-plane shear deformation vibrations of the methylene groups in the polymer backbone retains its position at 1456.26 cm^{-1}. In the regions of 1249.87 and 1136.07 cm^{-1}, valence vibrations of C-O bonds and deformation vibrations of the polymer matrix are observed. The increased intensity of the bands corresponding to the skeletal C–C bond vibrations and the in-plane deformational vibrations of the –CH groups at 1074.35 and 1029.99 cm^{-1} is due to the superposition of signals from the polymer backbone and the associated salts. Out-of-plane fan-shaped vibrations of -CH groups and pendulum vibrations of $–CH_2$ groups are observed in the low-frequency region at 881.47 cm^{-1}.

The synthesis of grinding intensifiers based on methyldiethanolamine and triethanolamine was carried out using various ratios of GIPAN+MDEAs or GIPAN+TEAs-1:1, 1:0.5, and 1:9-depending on the reaction temperature and time, with the aim of identifying the optimal ratio of starting materials. Figure 2 shows the graphical dependence of the yield of the HIPAN+MDEAs-based intensifier on temperature (a) and time (b).

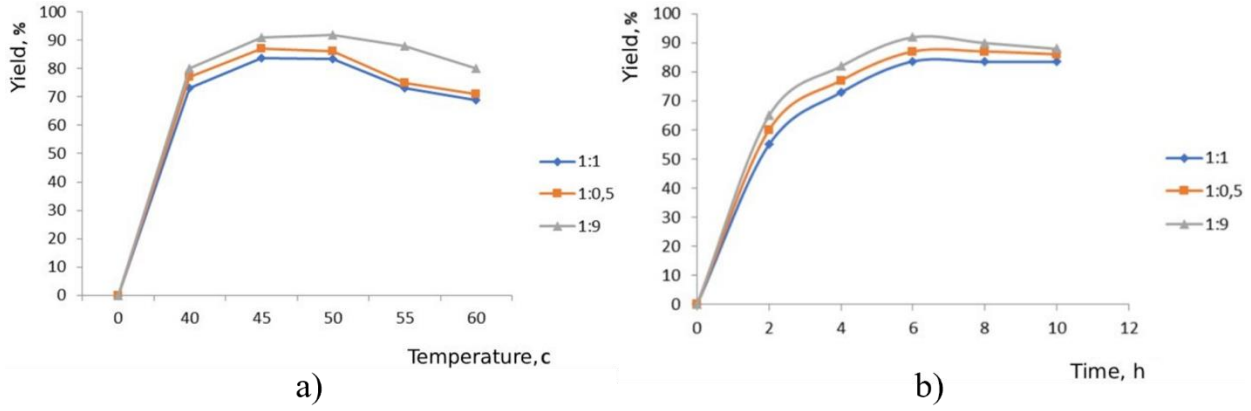


Fig. 2. Dependence of the yield of the GIPAN+MDEAs-based intensifier on temperature (a) and time (b)

As shown in Figure 2, the optimal conditions for producing an intensifier based

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on GIPAN+MDEAC are a reaction temperature of 40 0C for 6 hours, with a component ratio of 1:9. The product obtained under these conditions is highly effective.

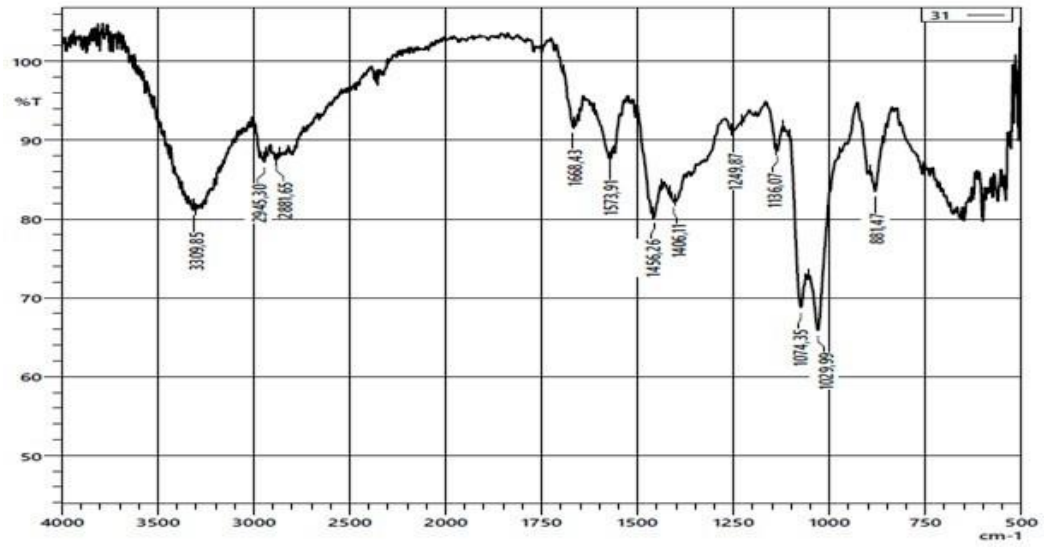


Fig. 3. IR spectrum of GIPAN+MDEAC at a 1:9 ratio

The IR spectrum of the GIPAN+MDEA mixture (1:9 ratio) is characterized by a pronounced superposition of the spectral features of both components, with the amino alcohol bands predominating (Fig. 3). The high MDE content is confirmed by the extremely high intensity of the valence vibration doublet of the alcohol C–O bonds at 1074.35 and 1029.99 cm^{-1}, as well as a broad band associated with hydroxyl O–H groups at 3309.85 cm^{-1}. The polymeric matrix of GIPAN is identified by the bands of valence asymmetric and symmetric vibrations of the carboxylate groups – COO^- (1573.91 and 1406.11 cm^{-1}, respectively) and the carbonyl (C=O) band of residual amide units (1668.43 cm^{-1}). Valence and deformation vibrations of the aliphatic CH_2-, CH_3-, and CH-groups appear in the regions of 2945–2881 cm^{-1} and 1456.26 cm^{-1}, while weak signals from the C–N bonds of the tertiary amine appear in the range of 1250–1136 cm^{-1}".

Table 1. Physicochemical Properties of the GIPAN+MDEAC-Based Intensifier

Name of Indicators	
Appearance	A reddish-coloredliquid
Density at 20°C, not less than	1,2
Mass fraction of water, %—not to exceed	3,0
Hydrogen ion activity (pH) of a 2.5% aqueous solution	9,0 ±1,0
Mass fraction of chloride ions in dry matter, %, not more than	0,001
Solubility in water at 20 ^{0}C, g/100 g of water	22

The determined physicochemical parameters of the developed grinding intensifier (Table 1) are directly related to its molecular structure, the nature of which is revealed in detail by analysis of the IR spectrum of the GIPAN+MDEAs composite system (Fig. 3).

Thus, the dominance of methyl

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diethanolamine signals in the spectrum (at a 1:9 ratio) and the pronounced presence of the bands of asymmetric and symmetric valence vibrations of carboxylate anions (-COO-) at 1573.91 and 1406.11 cm^{-1} confirm the stable existence of the salt form of GIPAN. The presence of protonated and ionized centers in the system necessitates a strictly controlled alkaline environment (pH 9.0 ± 1.0), which is crucial for the passivation of metal surfaces in cement mill equipment.

The intensifier's high water solubility (22 g per 100 g of water) and stable retention of residual moisture at a level of no more than 3.0% are due to the strong hydrophilicity of the polymer matrix and the amino alcohol. This is clearly confirmed by the detection of an intense broadened band at 3309.85 cm^{-1} (overlap of the vibrations of the associated –OH groups of MDE, molecular water, and –NH bonds), as well as by the anomalous increase in intensity and splitting of the valence vibration bands of the C–O bonds of the primary alcohol groups (–CH_2–OH) of the excess MDE in the regions of 1074.35 and 1029.99 cm^{-1}. The presence of such a dense network of hydrogen bonds and polar fragments makes the synthesized product a stable, homogeneous concentrate suitable for precision spray dosing in clinker grinding processes.

The synthesis process of the grinding intensifier based on GIPAN+TEA as a function of reaction time and temperature is shown in Figure 4.

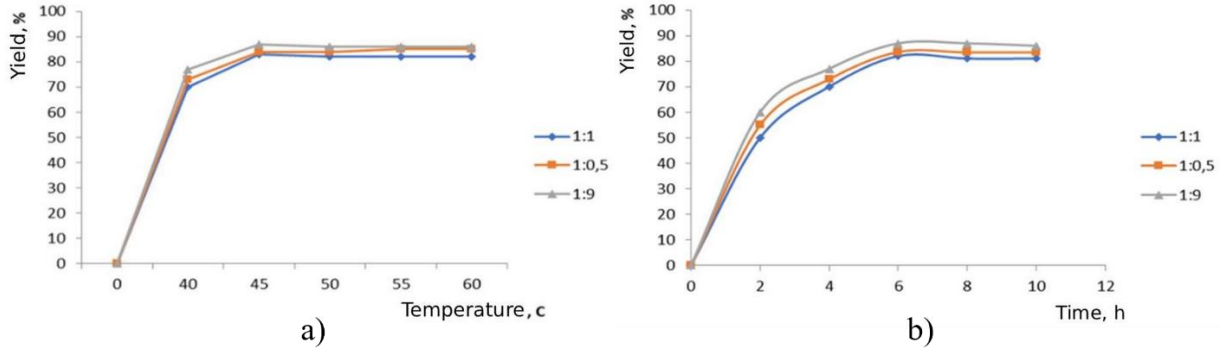


Fig. 4. Dependence of the output of the GIPAN+TEA-based intensifier on temperature (a) and time (b)

As shown in Figure 4, an 87% yield of the intensifier is obtained when the reaction is carried out under optimal conditions for 6 hours. Continuing the reaction under these conditions leads to a decrease in product yield. This is due to the intensification of parallel reactions (such as cross-linking, decomposition, intermolecular interactions, etc.), which reduce the intensifier's effectiveness. Thus, the optimal conditions for producing the GIPAN+ TEA-based intensifier are a reaction temperature of 45 ^{0}C for 6 hours, with a component ratio of 1:9. The product obtained under these conditions exhibits a very good effect.

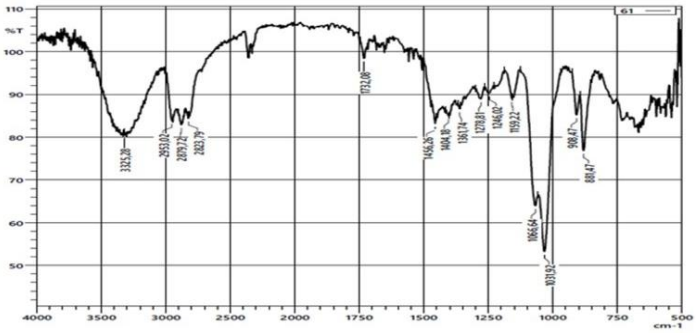


Fig. 5. IR spectrum of GIPAN + TEA at a 1:9 ratio

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The spectral profile of the GIPAN+TEA (1:9) mixture is primarily determined by the absorption bands of triethanolamine, which mask part of the signals from the polymer matrix (Fig. 5). The high TEA content is evidenced by a strong doublet of valence vibrations of the alcohol C–O bonds at 1066.64 and 1031.92 cm^{-1} and a broad hydroxyl O–H band at 3325.28 cm^{-1}. A specific feature of TEA is the triplet of valence vibration bands of C–H bonds in the 2953–2823 cm^{-1} region, where the peak at 2823.79 cm^{-1} indicates the presence of $–CH_2–N=$ bonds. The contribution from the GIPAN group is identified by the weak bands of the carboxylate ions $–COO^-$ (1456.26 and 1404.18 cm^{-1}) and the carbonyl group C=O band at 1732.08 cm^{-1}. The bands of C–N valence vibrations in the amine and the deformation vibrations of the CH_2 groups are observed in the ranges of 1361–1159 cm^{-1} and 908–881 cm^{-1}, respectively.

Table 2. Physicochemical Properties of the GIPAN+TEA-Based Intensifier

NameofIndicators	
Density at 20°C, not less than	Whitepowder
Mass fraction of water, %-not to exceed	1,17
Hydrogen ion activity (pH) of a 2.5% aqueous solution	3,0
Mass fraction of chloride ions in dry matter, %, not more than	9,0 ±1,0
Solubility in water at 20 ^{0}C, g/100 g of water	0,001
Density at 20°C, not less than	25

An analysis of the physicochemical properties of the synthesized GIPAN+TEA-based intensifier (Table 2), combined with IR spectroscopy data (Fig. 5), allows us to establish a relationship between the macroscopic properties of the resulting solid-phase product and its molecular structure.

The transition of the intensifier to a solid state (white powder) with a bulk density of at least 1.17 g/cm3 is due to the formation of a branched and robust three-dimensional network of intermolecular ionic and hydrogen bonds between the GIPAN polymer matrix and TEA molecules. In the IR spectrum of the composition (Fig. 5), this is reflected in the shift and strong broadening of the valence vibration band of the associated hydroxyl (–OH) and amide (–NH) groups, which is observed in the high-frequency region with a maximum at 3325.28 cm^{-1}. The high concentration of these hydrophilic polar centers, as well as the strong contribution of asymmetric and symmetric valence vibrations of the C–O bonds in the TEA alcohol fragments (an intense split peak at 1066.64 and 1031.92 cm^{-1}), determine the powder's excellent solubility in water-up to 25 g per 100 g of water at 20 °C.

The stable value of the hydrogen ion activity (pH = 9.0 ± 1.0) for a 2.5% aqueous solution of the additive is explained by the formation of the salt form. This is confirmed by the presence of absorption bands of carboxylate anions (–COO-) of GIPAN at 1404.18 cm^{-1} (symmetric vibrations), which interact with the protonated tertiary amino groups of TEA (valence vibrations of the aliphatic C–N bonds are observed at 1159.22 cm^{-1}). A weak band at 1732.08 cm^{-1} corresponds to residual carbonyl groups (C=O) in undissociated or ester fragments.

The combination of the identified characteristics—a strongly alkaline solution (pH ~ 9.0), a high content of the main substance (water mass fraction not exceeding 3.0%), and the virtually complete absence of corrosive chloride ions (≤ 0.001%) - characterizes the resulting chloride-free powdered intensifier as a technologically effective and safe component for intensifying the dry grinding of cement clinker.

A comparative analysis of Fourier transform infrared (FTIR) spectra at various stages of polymer matrix modification allows

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for a detailed tracking of the dynamics of successive chemical transformations from the initial PAN raw material to "GIPAN+amino alcohol" composite systems. The transition from the initial PAN to the hydrolyzed product (GIPAN) is accompanied by the complete disappearance of the characteristic narrow peak of the nitrile groups (–CN) in the region of ~2243 cm^{-1}, which conclusively proves the complete conversion of the initial units during the alkali saponification process. The formation of the target salt structure of sodium polyacrylate is experimentally verified by the appearance of a high-intensity characteristic doublet at 1573.91 and 1406.11 cm^{-1}, corresponding to the asymmetric and symmetric valence vibrations of the carboxylate anions ($–COO^–$), as well as by the preservation of the Amide I band (1668.43 cm^{-1}) of the intermediate amide fragments.

The subsequent introduction of MDEAs and TEAs as intensifying additives in a significant excess (mass ratio of 1:9) leads to a substantial transformation of the spectral profile due to the superposition and dominance of signals from low-molecular-weight amino alcohols, which partially mask the bands of the polymer matrix. The main spectral feature of both mixed systems is an anomalous equivalent increase in intensity and band splitting in the region of 1074–1029 cm^{-1} (for MDE) and 1066–1031 cm^{-1} (for TEA), caused by valence vibrations of the simple C–O bonds of primary alcohol hydroxyl groups ($–CH_2–OH$). The specific nature of intermolecular interactions and structural differences among the introduced amino alcohols are most clearly evident in the region of aliphatic valence vibrations of C–H bonds (2953–2823 cm^{-1}): in the GIPAN+TEA system, a unique triplet with a clearly differentiated peak at 2823.79 cm^{-1} is observed, corresponding to the vibrations of methylene groups in the α-position relative to the tertiary nitrogen atom ($–CH_2–N=$), whereas this band is absent in the less branched MDEA molecule. The observed band overlap effects, bathochromic shifts of the hydroxyl and carboxylate group maxima (shift of the $–COO^–$ bands in TEA to 1456.26 cm^{-1}) collectively confirm the high degree of molecular compatibility of the components, due to a well-developed system of intermolecular hydrogen bonds between the functional groups of GIPAN and hydroxyalkylamines."

Results of chromatography-mass spectrometry analysis of the starting materials and synthesized products.

Chromatography-mass spectrometry (CMS) was used to identify the composition of multicomponent secondary feedstocks in the oil and gas industry, as well as to assess the extent to which hydrolysis and esterification reactions had occurred.

In the first stage of the research, GC-MS was used to study the qualitative and quantitative composition of desulfurization waste from hydrocarbon feedstocks used as amine modifiers. Analysis of individual mass spectra based on the mass-to-charge ratio (m/z) of fragment ions showed that the secondary products under study constitute a complex mixture of aliphatic amino alcohols. The main components of the mixture are triethanolamine (TEA) and methyldiethanolamine (MDEA), with trace amounts of mono- and diethanolamines, as well as trace amounts of associated hydrocarbon radicals. Peak identification using international mass-spectrum libraries confirmed the high suitability of these process wastes for creating synergistic grinding intensifier compositions without the need for prior deep rectification.

In the second stage, the HMC method was used to analyze the mother liquors and volatile fractions formed during the acid etherification of hydrolyzed polyacrylonitrile with methanol. Mass spectrometric monitoring of the fractionation confirmed that, during the washing of the synthesized polycarboxylate ether in a Buchner funnel, the unreacted excess methanol, trace amounts of free ethanolamines, and low-molecular-weight volatile byproducts are completely removed.

The combined data from chromatography-mass spectrometry and IR spectroscopy conclusively demonstrate that the developed method for isolating and purifying the precipitate allows for the

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production of the target polycarboxylate grinding intensifier in a high-purity state, free from toxic organic impurities, which is extremely important for its subsequent safe industrial application in cement technology.

To assess the potential effectiveness of the synthesized additives, a comparative analysis was conducted of their chemical structure and spatial configuration, which determine the nature of the adsorption interaction with the juvenile surface of cement clinker.

The main theoretical and structural differences between the developed compositions (GIPAN+MDEAs) and (GIPAN+TEAs) are presented in Table 3.

Table 3. Physicochemical and structural characteristics of the amino modifiers in the compositions

Characteristics of	Methyldiethanolamine (MDEA)	Triethanolamine (TEA)
Chemical formula	CH3N(CH2CH2OH)2	N(CH2CH2OH)3
Number of hydroxyl groups (–OH)	2	3
Spatial Stereometry	Compact, plane-oriented	Branched, three-rayed ("umbrella-shaped")
Dominant peaks in the IR spectrum (C–O)	Averageintensity (1074, 1029 cm^{-1})	Extremeintensity (1066, 1031 cm^{-1})

Based on a comparison of molecular structure and spectral data, key theoretical aspects have been identified that determine the synergism between GIPAN and each of the alkanolamines: the advantage of TEA lies in its adsorption energy and the density of its hydrogen bonds.

As shown in the IR spectrum of the "GIPAN + TEA" sample, the absorption bands in the 1066–1031 cm^{-1} region exhibit tremendous intensity, which is due to the presence of three hydroxyethyl groups in the TEA molecule. Upon adsorption on clinker, triethanolamine is capable of forming a denser network of coordination and hydrogen bonds with metal ions (Ca2+, Al3+, Fe3+) and silicate units. This theoretically results in a higher two-dimensional wedging pressure at the mouths of microcracks (the Rebinder effect) during the initial stages of solid-body deformation.

The advantages of MDEA lie in its diffusion kinetics and steric barrier.

The MDEA molecule has a lower molecular weight and more compact spatial dimensions due to the replacement of one hydroxyethyl group with a methyl radical (–CH3). Thanks to their high mobility and lower steric (spatial) barriers, MDEAs are able to diffuse more rapidly into the ultra-thin microcracks of cement particles during dynamic grinding. The IR spectrum of the GIPAN + MDEAC composition shows a shift in the valence vibrations of the –CH bonds (2945 cm^{-1}), which confirms the conformational flexibility of the methyl radical, contributing to the hydrophobization of the outer layer of the solvate shell.

The GIPAN + TEA system forms a more powerful steric barrier due to the pronounced three-arm geometry of the TEA molecules. The long chains of GIPAN, combined with the bulky "umbrella-shaped" TEA molecules, effectively shield the dispersed particles, preventing them from coming closer together under the influence of van der Waals forces.

The GIPAN + MDEAC system, due to the increased basicity of the tertiary nitrogen bonded to a methyl group, effectively neutralizes excess electrostatic charges on clinker fragments, acting primarily as an electrostatic deagglomerato.

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4 CONCLUSION

Using recycled polyacrylonitrile fiber (from old carpet products made from nitrocellulose fiber) as a polymer feedstock, a targeted two-stage synthesis was carried out to produce an effective polymer matrix for cement grinding intensifiers. The method involves controlled 8% alkaline hydrolysis of PAN followed by acid esterification with methanol to produce water-soluble polycarboxylate esters.

New import-substituting composite formulations for cement grinding intensifiers have been developed by combining the synthesized polymer matrix with secondary amine alcohols (oil and gas refining waste products)-methyldiethanolamine (MDEA) and triethanolamine (TEA)-in a mass ratio of 1:9.

The extent of the chemical transformations was rigorously demonstrated using Fourier-transform infrared spectroscopy: the complete disappearance of the PAN nitrile group peak (2243 cm-1) and the appearance of intense characteristic bands of carboxylate anions (1573 and 1404 cm-1), amide (1668 cm-1), and ether fragments. Chromatographic-mass spectrometric analysis confirmed the high purity of the isolated polymer (yield 31.2 g) and the multicomponent synergistic composition of the amino waste materials used.

A step-by-step physicochemical mechanism of action for the developed additives has been formulated, based on the Rebinder effect (adsorption-induced reduction in clinker strength). It has been established that the composition with TEA forms a stiffer steric barrier due to its three-ray geometry, whereas the system with MDEAC exhibits enhanced kinetic diffusion ability into ultrathin microcracks. The use of these additives theoretically justifies the prevention of cement particle aggregation and re-grinding, which opens up broad prospects for resource conservation in the cement industry.

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Kasimova Guzal Anvarovna– Preparation, in particular comments or revision, including the stages before or after publication (including translation, in essence);
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