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ЗАКОНОМЕРНОСТИ МЕХАНОХИМИЧЕСКОЙ ГИДРОФОБИЗАЦИИ МОНОАММОНИЙФОСФАТА

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В работе исследовано влияние механической обработки на гидрофобизацию моноаммонийфосфата (МАФ) кремнийорганической жидкостью и диоксидом кремния с целью получения основного компонента многоцелевых огнетушащих порошков. Определены гидрофобные свойства смесей различного состава. На основании полученных результатов установлено оптимальное содержание гидрофобизиующих агентов для получения моноаммонийфосфата с наилучшими гидрофобными свойствами. Показано, что использования при механохимической гидрофобизации МАФ только кремнийорганической жидкости не достаточно для достижения необходимых показателей по способности к водоотталкиванию, склонности к слеживанию, насыпной плотности и фракционному составу. Согласно ГОСТ Р 53280.4-2009, способность к водоотталкиванию (порошки не должны полностью впитывать капли воды) должна составлять не менее 120 мин; склонность к слеживанию (масса образовавшихся комков) не должна превышать 2 % от общей массы образца; кажущаяся плотность неуплотненных и уплотненных порошков должна быть не менее 700 и 1000 кг/м^3, соответственно. Установлено, что для достижения заданных параметров механохимическая гидрофобизация моноаммонийфосфата должна включать модифицирование смеси состава: 95 мас. % фосфата аммония, 4,5 мас. % диоксида кремния и 0,5 мас. % гидрофо-бизирующей жидкости в мельнице с ударно-сдвиговым характером нагружения при величине подводимой энергии 100-110 Дж/г. Отсутствие влаги в сырье (предварительная сушка частиц МАФ) позволяет получить более мелкодисперсный продукт с низкой склонностью к влагопоглощению. Процесс механохимической гидрофобизации МАФ заключается в том, что гидрофобизированный диоксид кремния при измельчении покрывает частицы моноаммонийфосфата, вследствие чего происходит блокирование активных центров адгезии и создается структурно-механический барьер, препятствующий агрегации частиц.

Ключевые слова: моноаммонийфосфат, гидрофобизация, механохимическое модифицирование, диоксид кремния, измельчение

MECHANOCHEMICAL HYDROPHOBIZATION OF MONOAMMONIUM PHOSPHATE

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Here, we investigated the influence of mechanical treatment on hydrophobization of monoammonium phosphate (MAP) with organosilicon liquid and silicon dioxide in order to obtain the main component of multipurpose fire extinguishing powders. We estimated hydrophobic properties of mixtures of various compositions. Based on the obtained results, the optimal content of hydrophobizing agents for obtaining monoammonium phosphate with the best hydrophobic properties was established. It is shown that the use of only organosilicon liquid for mechanochemical hydrophobization of MAP is not enough to achieve required values for water repellency, tendency to

aggregation, bulk density and particle size distribution. According to GOST R 53280.4-2009, the ability to repel water (powders should not completely absorb water droplets) should be at least 120 min; the tendency to caking (mass of the formed aggregates) should not exceed 2% of the total mass of the sample; the apparent density of uncompacted and compacted powders should be at least 700 and 1000 kg/m^3, respectively. It was found that in order to achieve the specified parameters, the mechanochemical hydrophobization of monoammonium phosphate should include modification of the mixture which contains 95 wt. % ammonium phosphate, 4.5 wt. % silicon dioxide and 0.5 wt. % hydrophobizing organosilicon liquid (HOL) in a mill with shock-shear loading at an input energy of 100-110 J/g. The absence of moisture in the raw material (preliminary drying of MAP particles) allows us to obtain a finer-grained product with a low tendency to moisture absorption. The process of mechanochemical hydrophobization of MAP can be described in the following way. During grinding hydrophobized silicon dioxide covers the particles of monoammonium phosphate, resulting in blocking active centers of adsorption and creating a structural and mechanical barrier that prevents particle aggregation.

Key words: monoammonium phosphate, hydrophobization, mechanochemical modification, silicon dioxide, grinding

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INTRODUCTION

Nowadays, one of the most commonly used fertilizers for agriculture is monoammonium phosphate (MAP, ammophos). It is a complex fertilizer that contains two major elements – phosphorus and nitrogen. The amount of industrially produced MAP are annually increasing due to its sharp consumption growth. One of the alternative areas where MAP finds broad application is fire safety industry where it is used as a component of fire extinguishing powders. It is well known that ammonium phosphate forms a film that covers the burning surface preventing further oxygen supply to the ignition place. Moreover, chemicals releasing as a result of monoammonium decomposition break down chemical chain reactions in fire. In spite of its fire preventing properties ammonium phosphate in the form of fine powder does not match the main technical requirements for fire extinguishing powders (FEP) such as fire extinguishing efficiency, apparent bulk density, moisture adsorption and caking tendencies, water-repellency ability, humidity and fluidity. All these characteristics depend on the properties of raw materials, and how they are processed. Previous results show that chemically pure monoammonium phosphate, which contains the minimum concentration of ammonium fluoride and magnesium phosphate perform better as a component of fire extinguishing mixtures in comparison to the MAP containing additives [1].

The production technology of FEP where phosphates are the main component is based on mechanical grinding. It is important to note that the final properties of FEP depend on grinding time or, more accurately, the amount of energy supplied [2]. As authors show in [3], there is an optimal time for mechanical grinding, or amount of energy supplied. To achieve desired properties of the final product, various additives can be added to the mixture. These additives can be hydrophobic, anti-caking, and weighting. In the previous work [4], authors found out that addition of hydrophobizing liquid and finely dispersed silica improves physicochemical properties of monoammonium phosphate.

Therefore, the objective of this work is to understand the influence of adding organosilicon liquids and highly dispersed silica on hydrophobic properties of ammonium phosphate, in particular, moisture adsorption capacity, when they are all mechanically activated together, and to determine the optimal composition of FEP that best fulfill the requirements of Russian standard GOST R 53280.4-2009.

MATERIALS AND METHODS

In the paper the following substances were used;

1. Monoammonium phosphate, reagent grade (GOST 3771-74). Mass fraction of MAP is not less than 99.5 wt.%.

2. Amorphous silicon dioxide (SD), grade WS-120 (white soot, GOST 18307-78). Mass fraction of

silicon dioxide is not less than 87 wt.%, water content does not exceed 6.5 wt.%, and the rest are impurities.

3. Hydrophobizing organosilicon liquid (HOL), grade 136-41 (GOST 10834-76). The main component is polymethylhydridesiloxane (PMHS).

Some samples of MAP were preliminary dried at 60 °C until the constant weight is reached. The amount of added organosilicon liquid was varied from 0.5 to 5.0 wt.% while the amount of white soot was varied from 4.5 to 5.0 wt.%. Mechanochemical hydrophobization of ammonium phosphate was carried out by adding the modifiers listed above at the destruction moment of the main component (MAP reagent grade) when it is grinded in a roller-ring vibrating mill VM-4 with energy supply of 0.878 kW/kg. Moisture adsorption tendency of the obtained powder was determined as a mass change of the sample when keeping it in a desiccator at a constant humidity. Water-repellency ability was determined by visual assessment as a time required for water droplets being absorbed by powder. Bulk density was calculated as the ratio of mass of the powder freely filled into a cylinder to the volume that the powder occupies. IR spectra were measured with diffuse reflection using the atmospheric compensation mode in a Bruker Optics Tensor 27 spectrometer. The SEM images were obtained with JSM-6460 LV microscope. The solubility of MAP was assessed by measuring concentration of P_2O_5, N, and SO_3 in aqueous solutions or suspensions of prepared samples.

RESULTS AND DISCUSSION

In order to estimate hydrophobization efficiency we use the following criteria: water-repellency ability, tendency to caking, bulk density and fractional composition. Tables 1 and 2 show how the presence of free moisture and the amount of additives influence the efficiency of hydrophobization of monoammonium phosphate. We find out that if the amount of introduced hydrophobizer varies within the range of 0-5 wt. %, moisture adsorption tendency decreases from 3.3 to 1.3%, and water-repellency capacity increases from 0 to 360 min (Table 2, samples 1-5). In addition, introduction of HOL at concentrations of 5-7 wt. % to monoammonium phosphate significantly decreases its solubility in water (Fig. 1).

To study hydrophobic properties of modified MAP, we prepare 15 samples with various amounts of monoammonium phosphate, HOL and silicon dioxide (Table 1).

Table 1

Composition of initial powder mixtures and their bulk densities

***Таблица 1.* Состав исходных порошковых смесей и их насыпная плотность**

№	Composition (wt. %)			Bulk density, g/cm^3	
	MAP	HOL	SD	compacted	uncompacted
1	100.0	0.0	0.0	822	476
2	99.5	0.5	0.0	989	511
3	99.0	1.0	0.0	862	543
4	98.0	2.0	0.0	908	605
5	95.0	5.0	0.0	936	754
6	95.0	0.0	5.0	948	499
7	95.5	0.5	4.5	936	498
8*	100.0	0.0	0.0	821	420
9*	99.5	0.5	0.0	960	479
10*	99.0	1.0	0.0	857	454
11*	98.0	2.0	0.0	910	518
12*	95.0	5.0	0.0	957	708
13*	95.0	0.0	5.0	1002	501
14*	95.0	0.5	4.5	962	562
15	95,0	0,0	5,0**	953	555

Notes: * – MAP samples were dried at 60 °C up to constant weight;
** – mechanically modified SD
Примечания: * - образцы МАФ сушили при 60 ° С до постоянной массы;
** - БС механически модифицированная

According to [5] the preferred size of particles used to prepare fire extinguishing powders should not exceed 50 μm. The amount of added HOL to MAP should be carefully determined in order to achieve the best performance of FEP. For example, if the concentration of HOL in MAP exceeds the optimum value, then, the yield of 50 μm fraction significantly reduces from 90.4 to 11.3% (Table 3, samples 2-5). In this case, layering of the hydrophobizing film is observed (the so-called oiling effect). The interaction of free molecules of PHMS between each other [6] leads to adhesion of particles and their aggregation resulting in formation of large agglomerates, as evidenced from an increase in the amount of fraction with the particle size larger than 1250 μm from 0.9 to 45.8% (Table 3, samples 2-5). Because of agglomeration, the bulk density of the powder increases from 862 to 936 g/cm^3 for the compacted and from 543 to 754 g/cm^3 for the uncompacted powders (Table 1, samples 3-5). The highest bulk density for the compacted powder, equal to 989 g/cm^3, has the sample containing 0.5 wt. % of HOL (Table 1, sample 2). In this case, formed fine particles occupy free space between bigger particles, thus, reducing the occupied volume.

Table 2

Hydrophobic properties of the obtained powder mixtures after mechanical activation

***Таблица 2.* Гидрофобные свойства смесей после механической активации**

№	Moisture adsorption tendency, wt. %	Water-repellency ability, min., from the moment of obtaining the powder	
		0 hr.	24 hr.
1	3.3	0	0
2	2	0	110
3	1.9	0	150
4	1.4	0	195
5	1.3	0	360
6	3.4	0	0
7	0.9	More than 180	630
8*	0.9	0	0
9*	1.8	0	56
10*	1.6	0	100
11*	1.5	0	175
12*	1.3	0	300
13*	2.3	0	0
14*	0.5	More than 180	530
15	2.3	-	150

Table 3

Change in the fractional composition of powder mixture when grinding MAP with HOL and SD in the mill

***Таблица 3.* Изменение фракционного состава при измельчении МАФ «хч» с ГКЖ 136-41 и БС-120 в вибро-мельнице**

№	Fraction amount, %						
	Particles size of fraction, μm						
	>1250	630-1250	315-630	140-315	100-140	50-100	<50
1	35.7	12.5	12.3	8.8	3.9	0.2	26.6
2	0.9	1.3	1.3	5.2	0.1	0.8	90.4
3	3.1	2.8	2.2	8.8	5.3	20.9	56.9
4	11.4	4.8	9	23.1	7.9	12.7	31.1
5	45.8	10.3	12.5	10.1	1.8	8.2	11.3
6	0	0	0.2	1.3	0.7	11.4	86.4
7	0	0.1	0.3	0.4	0.2	1.5	97.5
8	4.3	11.2	14.8	16	5.1	2.8	45.8
9	1.1	1	0.8	1.1	0.3	1.5	94.2
10	0.1	3.6	1	0.9	1.8	0.2	92.4
11	0.4	1.3	2.4	14.1	12.2	0.8	68.8
12	39.7	9.9	12.5	11.5	7.7	0.2	18.5
13	0	0	0.2	1.4	1.9	19.9	76.6
14	1.3	1.1	1.1	0.5	0.2	0.6	95.2
15	0	0	0.3	0.4	0.3	0.6	98.4

We observe an increase in the number of particles with the size of 50 μm from 26.6 to 86.4% if 5 wt. % of SD is added to MAP. At the same time, there is no aggregation on the walls of the mill, and moisture adsorption tendency remains constant (3.3 and 3.4%) for samples 1 and 6 in Table 2.

Since the SD has high specific surface area equal to 120 g/cm^2, the hydroxyl groups located on the surface tend to interact with atmospheric moisture through hydrogen bonding. Thus, the product containing MAP, SD and HOL, has water-repellency ability of 630 min, and contains 97.5% of particles with the size less than 50 μm (Tables 2 and 3, sample 7). It should be noted that efficiency of the hydrophobization process improves if free moisture present on the surface of monoammonium phosphate particles is removed. Absence of moisture in raw material makes it possible to obtain finely dispersed product with low moisture adsorption tendency (Tables 2 and 3, samples 8-14).

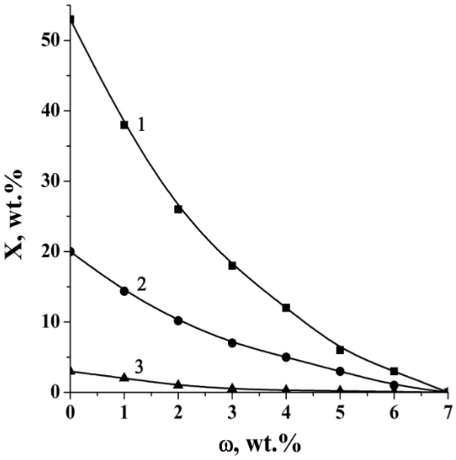
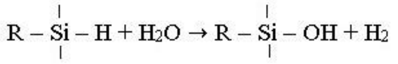


Fig. 1. Concentration of P_2O_5 (1) (X, wt. %), N (2), SO_3 (3) in the liquid phase containing dissolved ammonium phosphate as a function of the amount of introduced hydrophobizer (ω, wt. %)

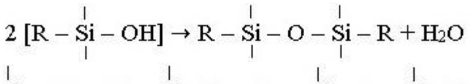
Рис. 1. Изменение содержания P_2O_5 (1) (X, мас. %), N (2), SO_3 (3) в жидкой фазе при растворении фосфата аммония от количества вводимого гидрофобизатора (ω, мас. %)

In spite of this, the hydrophobized powder based on MAP kept in air, has greater water-repellency ability. Sample 7 has a much higher water-repellency ability, than sample 14 (Table 2), while the amount of the fraction smaller than 50 μm and the moisture adsorption tendency have negligible difference – 97.5% and 95.2% (Table 2), 0.9 and 0.5% (Table 3), respectively. It is possible that water molecules on the surface of the water-soluble salt react with PMHS leading to hydrolysis of the Si-H bond. This process can be described by the following reaction [7]:

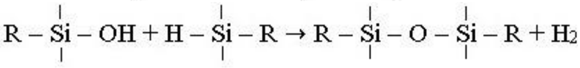


$$R - \overset{|}{\underset{|}{Si}} - H + H_2O \rightarrow R - \overset{|}{\underset{|}{Si}} - OH + H_2$$

Subsequent condensation leads to cross-linking of polysiloxane chains resulting in a single water-repellent film:



$$2\,[R - \overset{|}{\underset{|}{Si}} - OH] \rightarrow R - \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - R + H_2O$$



$$R - \overset{|}{\underset{|}{Si}} - OH + H - \overset{|}{\underset{|}{Si}} - R \rightarrow R - \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - R + H_2$$

Freshly ground monoammonium phosphate powder, modified only with HOL, has low water-repellency ability (Table 2, samples 2-5 and 9-12). Only after some time the surface of particle acquires water-repellent properties: 110-360 min for samples 2-5 and 56-300 min for samples 9-12. It is assumed that monoammonium phosphate interacts with HOL through adhesion forces. At the same time, grinding MAP with 4.5 wt. % SD and 0.5 wt. % HOL for 2 min (Table 1, samples 7, 14) yields the product which has high water-repellency ability of 530-630 min and low moisture adsorption tendency of 0.5-0.9%. Therefore, it can be assumed that silicon dioxide has a major effect on the effectiveness of hydrophobization of hygroscopic salts such as monoammonium phosphate.

Let us consider the process of mechanochemical modification of the three-component system (MAP-SD-HOL). PHMS interacts with the active surface of SD through chemisorption and physical adsorption. At the same time, large molecules of HOL adsorb on the surface of MAP particles due to weak physical forces. The hydrophobized silicon dioxide covers the monoammonium phosphate particles. Friction between hydrophobic silica and hydrophilic MAP causes electrostatic interactions between particles [8] – fine powder of silica covers surface active sites of MAP that carry electric charge.

Microphotographs (Fig. 2) clearly show that particles of hydrophobisers tend to stick to large particles of monoammonium phosphate. Hydrophobized SD forms a structural and mechanical barrier that prevents aggregation of particles. These phenomena are confirmed by a sharp increase in water-repellency ability from 0 to 530 and 630 min of samples 7 and 14, respectively (Table 2). However, there are unsatisfactory results of mechanical modification of the hygroscopic salt (Table 2 sample 15), which may occur in some cases. First, mechanical forces may destroy the hydrophobic layer of SD. Secondly, under the given conditions, there is no physicochemical interaction between the components of the mixture.

The hydrophobization mechanism presented above can be confirmed by analyzing the IR spectra of hydrophobizing agents (HOL and SD, Fig. 3) and the products of their interaction with monoammonium phosphate (Sample 7, Fig. 4). Table 4 lists functional groups and chemical bonds found in samples obtained with mechanochemical modification of MAP with silica and HOL. In comparison to pure materials, the IR spectrum of hydrophobized monoammonium phosphate does not contain bands corresponding to Si-H and Si-OH bonds. This indicates the formation of water repellent film on the surface of MAP consisting of Si-O-Si bonds.

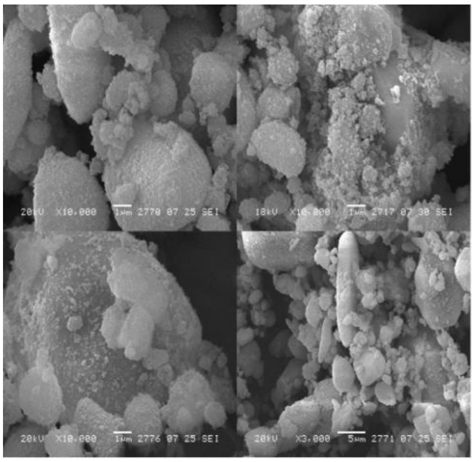


Fig. 2. Microphotographs of hydrophobized MAP with a HOL and SD content of 0.5% and 4.5% respectively
Рис. 2. Микрофотографии гидрофобизированного моноаммонийфосфата с содержанием ГКЖ 0,5% и БС 4,5%

Table 4

Typical types of bonds in hydrophobizing agents
***Таблица 4.* Характерные типы связей в гидрофобизирующих агентах**

PMHS (I)		SiO_2 (II)	
Wavenumber, cm^{-1}	Characteristic bond	Wavenumber, cm^{-1}	Characteristic bond
2966	C-H ($-CH_3$)	3631	$(Si-OH)_2$
2167	Si-H	3484	H-O-H
1261	$Si-CH_3$	1871	-OH (H_2O)
1100	Si-O-Si	1634	-OH (H_2O)
924	Si-H	1330	-OH (free)
893	Si-H	1188	Si-O-Si
841	$Si-CH_3$	1053	Si-O-Si
769	$Si-CH_3$	804	O-Si-O
437	Si-O-Si	528	Si-O-Si

CONCLUSIONS

In conclusion, it should be noted that for preparation of hydrophobic ammonium phosphate, the following conditions must be met:

1. Grinding and hydrophobization of the mixture containing 95 wt.% of ammonium phosphate, 4.5 wt.% of SD and 0.5 wt.% of HOL during 2 min at energy input value of 100-110 J/g;

2. The use of ammonium phosphate and silicon dioxide without their preliminary drying (humidity of SD - ≤1%, ammonium phosphate - ≤2%).

The obtained hydrophobized ammonium phosphate, containing 4.5 wt.% SD and 0.5 wt.% HOL, satisfies the requirements of GOST R 53280.4-2009: water-repellency ability (630-120 min) and moisture adsorption tendency (0.9-3.0%). In addition, the apparent bulk density of the prepared product is below the required value: 936-1000 and 498-700 kg/m^3 for the compacted and uncompacted powder, respectively.

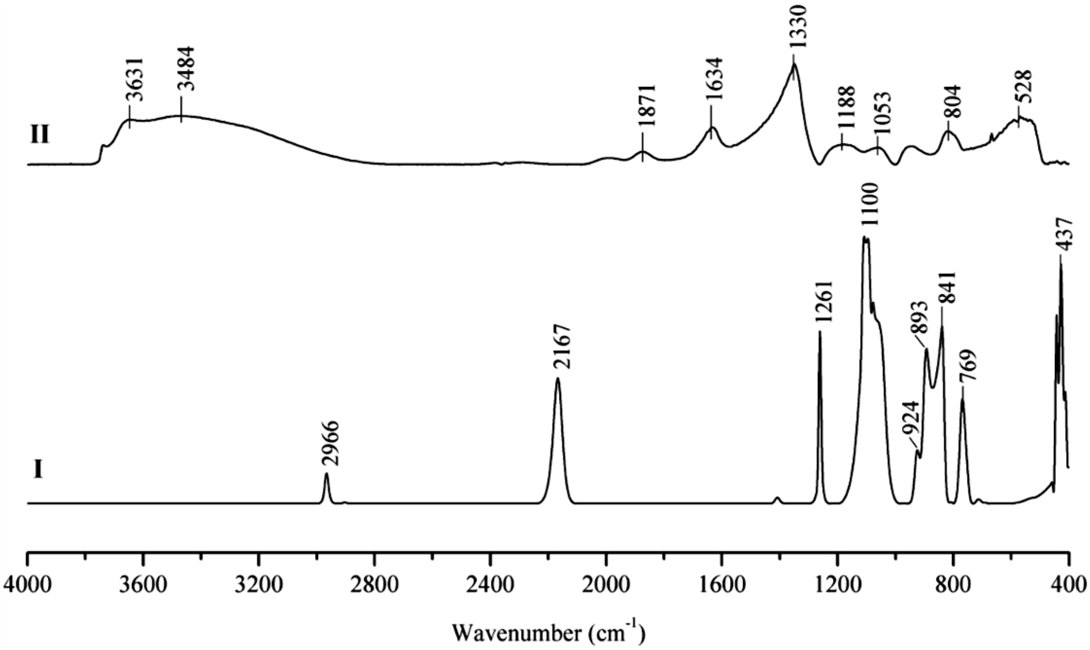


Fig. 3. IR spectra of hydrophobizing agents, I - HOL, II – SD

Рис. 3. ИК спектры гидрофобизирующих агентов, I – ГКЖ, II – БС-120

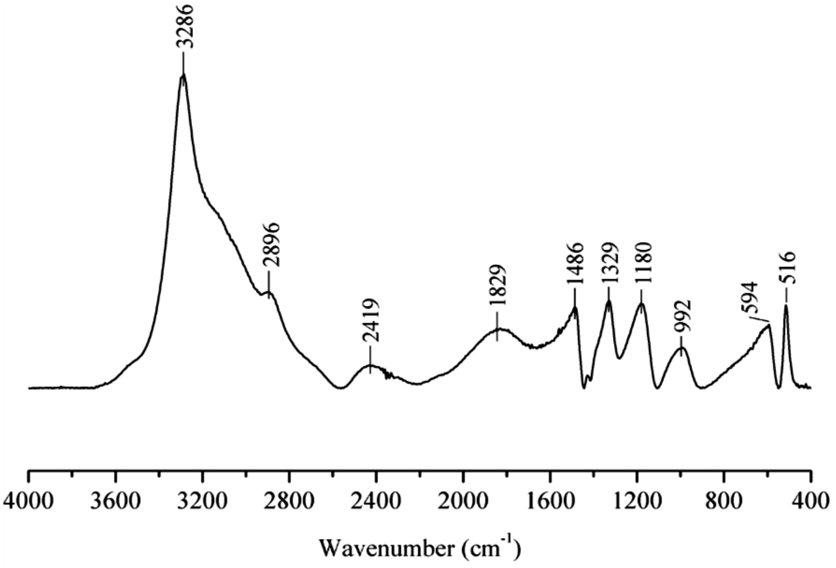


Fig. 4. IR spectrum of hydrophobized MAP with a HOL and SD content of 0.5% and 4.5% respectively

Рис. 4. ИК спектр гидрофобизированного моноаммонийфосфата с содержанием ГКЖ 0,5% и БС 4,5%

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