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Properties of Liquid Balanced NP-Fertilizers Based on Purified Ammophos Suspension and Ammonium Nitrate

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ABSTRACT: The composition and properties of liquid balanced NP-fertilizers based on purified ammophos suspension and ammonium nitrate ($N:P_2O_5$ = 1:0.5, 1:0.7 and 1:1) have been determined. The density and viscosity of liquid NP-fertilizers were studied at wide temperature ranges (30-80 ^oC). It is shown that with an increase in the $N:P_2O_5$ ratio from 1:0.5 to 1:1 and an increase in temperature from 30 to 80 °C, both the density and the viscosity decrease monotonically from 1.326 to 1.225 g/cm^3 and from 4.12 to 1.82 cPz, respectively. Specific conductivity of liquid NP-fertilizers for temperatures of 20-50 °C is 37.38-89.30 mS/cm. The vapor pressure over solutions of liquid NP-fertilizers was studied using the Claisus-Cliperon equation and empirical equations were derived using the least squares method.

KEYWORDS:extraction phosphoric acid, purified ammophos suspension, ammonium nitrate, liquid NP-fertilizers, composition, properties, density, viscosity, electrical conductivity, vapor pressure.

I. INTRODUCTION

In 2016, the global liquid fertilizer market was estimated at US $ 11,108 million, and by 2023 it is expected to reach US $ 13,530 million with an average annual growth rate of 2.8%. Currently, the key producers of liquid fertilizers are: Agrium Incorporated (Canada), Yara International ASA (Norway), K + S Aktiengesellschaft (Germany), Triangle Chemical Company (USA), Fox farm Fertilizer (USA), Compo Expert GmbH (Germany), Basf, Bayer, Dupont (Germany), Tessenderio Group (Belgium), Kugler Company (USA), Agro Liquid (USA), Plant Food Company (USA), countries of the Middle and Far East - Israel Chemical Ltd. (Israel), Haifa Chemicals Ltd. (Israel), Agro tiger (Turkey), Nutri-Tech Solutions (Australia). There are about 30 large manufacturers in the Russian agrochemical industry, the largest of which are CJSC PhosAgro AG, Uralkali OJSC Akron, AO-MHK EuroChem, OJSC UCC Uralchem [1].

According to the Food and Agriculture Organization, liquid fertilizers are used in more than 70 countries around the world. Basically, the dominant solutions are urea ammonium nitrate (UAN) and liquid ammonia (12.5 million tons and ~ 6.5 million tons). In the countries of North America (USA, Canada), the share of liquid fertilizers in the range of fertilizers is high (~ 35%), including 50% in the group of nitrogen fertilizers. The use of ammonia water in North America is insignificant (60-70 thousand tons in terms of N). In the countries of Western Europe, a high specific gravity of liquid ammonia, in France and Austria, UAN solutions are actively used [2].

The advantages of liquid fertilizers are: significantly lower capital costs due to the exclusion from the technological process of such energy-intensive operations as drying, granulation, classification, dust collection and

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operation of the return cycle; lack of caking, lumpiness and segregation in the processes of storage, transportation [3,4]. Whereas the loss of liquid fertilizers during handling and storage does not exceed 1%, and in the case of solid fertilizers this figure is 10-15% [5]. There are possibilities for dissolving and joint application of herbicides, insecticides, trace elements, growth substances, etc., with drip irrigation of agricultural crops, especially for greenhouses; better assimilation of macroelements by plants in comparison with solid fertilizers with insufficient soil moisture [6,7]. Especially liquid fertilizers have a positive effect on winter crops in critical periods of development, this is the tillering phase and the period before heading. In addition, nitrogen is absorbed through the leaf plate up to 80%, phosphorus and potassium - 50%. As for solid fertilizers, this figure is in the order of 40% for nitrogen and 15-20%, 40% for phosphorus and potassium [5,6,8,9]. It should be noted that on the calcareous soils of Uzbekistan with an alkaline reaction of the medium, the agrochemical value of liquid forms, as a rule, will be higher than that of granular ones.

Among experts in industry and agriculture, liquid complex fertilizers (LCF) containing two (N-P_2O_5) or three nutrients (N-P_2O_5-K_2O) were highly appreciated.

Concentrated phosphoric acid is mainly required for the production of liquid complex fertilizers [10]. It should be noted that using thermal (TPA) or one stripped off phosphoric acid (not less than 54% P_2O_5), an LCF of 8:24:0 composition is obtained, based on polyphosphoric (68-72% P_2O_5) - composition 10:34:0 and 11:37:0 [11,12].

Due to the lack of concentrated phosphoric acid, it is necessary to use standard extraction phosphoric acid (EPA) or its ammoniated solution instead of expensive thermal or superphosphoric acid. This requires the purification of EPA from impurities such as iron-aluminum phosphates, calcium and magnesium phosphates, fluoride compounds that reduce the quality of the finished product.

The purpose of this work is to obtain purified brands of NP-fertilizers by separating ammophos pulp into solid and liquid phases, followed by adding a nitrogen component to the filtrate obtained.

II. SIGNIFICANCE OF THE SYSTEM

The composition and properties of liquid balanced NP-fertilizers based on purified ammophos suspension and ammonium nitrate (N:P_2O_5 = 1:0.5, 1:0.7 and 1:1) have been determined.The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

To obtain NP fertilizers, EPA of the composition 16.46% P_2O_5, 0.06% CaO, 1.11% MgO, 0.27% Fe_2O_3, 0.41% Al_2O_3, 2.98% SO_3 and 0, 99% F and 100% NH_3. The process of neutralization of EPA was carried out with ammonia to a pH value of 4.51 to 6.56 at 65 °C. Then the ammophos slurry was separated into solid and liquid phases by centrifugation. The wet sediment was dried at 60 °C to constant weight and analyzed according to the procedures [13]. Various forms of phosphorus were determined photometrically. The assimilable forms of P_2O_5 were determined by their solubility in 2% citric acid. Nitrogen content in products according to Kjeldahl - distillation of ammonia in an alkaline medium with Devard's alloy, followed by titration.

Analysis of samples of the dried sediment shows that in all cases the maximum degree of transition of water-insoluble components (MgO - 88-89%, 86-88% Fe_2O_3, 83-89% Al_2O_3, 59-75% F) into the solid phase has been achieved. And the sediment containing a high content of total, assimilable and aqueous forms of phosphorus (46-47% P_2O_{5total}, $P_2O_{5acc.}$:P_2O_{5total} = 90-92% and P_2O_{5water}:P_2O_{5total} = 73-79%) is offered as an independent solid fertilizer - ammophos [14].

In order to obtain balanced NP-fertilizers of grades N:P_2O_5 = 1:0.5, 1:0.7 and 1:1 into the obtained filtrate of the composition (wt.%): 4.77-6.18% N, 14.05 -14.66% P_2O_5, 0.17-0.18% MgO, 3.64-4.07% SO_3, 0.37-0.5% F and 0.1-0.15% Fe_2O_3 + Al_2O_3 powders were introduced ammonium nitrate [15]. The compositions of the products are given in Table. 1..

IV. EXPERIMENTAL RESULTS

From Table 1 shown that with an increase in the amount of ammonium nitrate in the mixture, although the content of phosphorus decreases, without affecting the relative content of its assimilable form, the content of nitrogen increases. An increase in the pH of the ammophos suspension practically does not affect the relative content of the assimilable form of phosphorus, only slightly increases the content of its water-soluble form.

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Table 1
Composition of liquid balanced NP-fertilizers based on purified ammophos suspension and ammonium nitrate

Ratio of N : P_2O_5	Water content in slurry, %	Component content, wt.,%		$\frac{P_2O_{5ass.}}{P_2O_{5total}}$ %	$\frac{P_2O_{5water.}}{P_2O_{5total}}$ %	$T_{crystal.}$ °C
		$N_{total.}$	P_2O_{5total}			
Ammophos suspension with pH value = 4.51						
1 : 0.5	37.70	18.48	9.25	99.59	95.32	+23
1 : 0.7	45.43	14.85	10.40	99.7	95.42	+10
1 : 1	51.48	11.94	11.94	99.79	95.51	0
Ammophos suspension with pH value = 5.53						
1 : 0.5	39.70	17.74	8.87	99.69	96.95	+8
1 : 0.7	46.22	14.59	10.21	99.78	97.12	-5
1 : 1	52.80	11.78	11.78	99.84	97.51	-15
Ammophos suspension with pH value = 6.56						
1 : 0.5	40.29	17.90	8.95	99.91	97.55	+5
1 : 0.7	46.38	15.16	10.61	99.94	97.62	-8
1 : 1	54.04	11.97	11.97	99.96	97.89	-18

Transparent liquid fertilizers prepared on the basis of ammophos suspension with pH = 4.5; 5.5; 6.5 and dry NH_4NO_3 contain 17.90-18.48% N, 8.95-11.97% P_2O_{5total}, P_2O_{5water}.:P_2O_{5total}. = 95.32-97.55%, respectively, for the ratios N:P_2O_5 = 1:0.5; 1:0.7 and 1:1. Depending on the pH of the ammophos suspension and the N: P_2O_5 ratio, the crystallization temperature ($T_{crystal.}$) of the transparent liquid liquid fertilizer based on ammonium nitrate ranges from +23 to -18 ºC.

Further, the rheological properties of transparent LCF were studied depending on the pH of the ammophos suspension and the N:P_2O_5 ratio in the temperature range of 30-80 °C. The density of the pulps is by pycnometric method, and the kinematic viscosity is by means of the VPZh-1 capillary viscometer. The results are summarized in table. 2-3.

Table 2
Density of liquid NP-fertilizers based on purified ammophos pulp and ammonium nitrate

Ratio of N:P_2O_5	Density, g/cm^3 at temperatures, (° C)					
	30	40	50	60	70	80
Ammophos suspension with pH value = 4.51						
1 : 0.5	1.326	1.324	1.320	1.314	1.308	1.301
1 : 0.7	1.296	1.289	1.283	1.277	1.270	1.264
1 : 1	1.271	1.269	1.265	1.258	1.252	1.243
Ammophos suspension with pH value = 5,53						
1 : 0.5	1.324	1.321	1.317	1.312	1.306	1.299
1 : 0.7	1.293	1.287	1.281	1.274	1.268	1.262
1 : 1	1.268	1.266	1.262	1.256	1.250	1.241
Ammophos suspension with pH value pH = 6.56						
1 : 0.5	1.308	1.303	1.298	1.292	1.286	1.282
1 : 0.7	1.278	1.269	1.261	1.255	1.249	1.245
1 : 1	1.254	1.248	1.243	1.237	1.231	1.225

As it can be seen from them, with an increase in the N:P_2O_5 ratio from 1:0.5 to 1:1 and a temperature from 30 to 80 °C, both the density and the viscosity of liquid NP-fertilizers with pH = 6.56 decrease monotonically, then there is from 1.308 to 1.225 g/cm^3 and from 4.12 to 1.97 cPz.

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A similar phenomenon is observed for other pH values. For all brands of liquid NP-fertilizers, an increase in pH from 4.5 to 6.5 leads to an increase in both the density and viscosity of the suspensions, but they remain in a fluid state.

Table 3
Viscosity of liquid NP-fertilizers based on purified ammophos pulp and ammonium nitrate

Ratio of $N:P_2O_5$	Viscosity, cPz at temperatures, (° C)					
	30	40	50	60	70	80
Ammophos suspension with pH value = 4.51						
1:0.5	3.23	2.85	2.73	2.58	2.36	2.15
1:0.7	3.09	2.72	2.56	2.40	2.21	2.02
1:1	2.95	2.60	2.39	2.19	2.01	1.82
Ammophos suspension with pH value pH = 5.53						
1:0.5	3.88	3.30	3.00	2.66	2.41	2.17
1:0.7	3.71	3.16	2.82	2.47	2.26	2.05
1:1	3.54	3.01	2.63	2.26	2.05	1.84
Ammophos suspension with pH value pH = 6.56						
1:0.5	4.12	3.59	3.18	2.85	2.52	2.33
1:0.7	3.94	3.44	2.98	2.66	2.36	2.19
1:1	3.76	3.28	2.79	2.42	2.14	1.97

The specific electrical conductivity of liquid products was determined by the conductometric method in a glass resistance cell with platinum electrodes using a rheochord bridge in the temperature range 20-50 °C [16]. The potentiometer data (Ri, Ohm) was used to calculate the electrical conductivity $\chi = K/Ri$, where K is the cell constant.

The specific electrical conductivity of liquid balanced NP-fertilizers for temperatures of 20-50 °C was studied depending on the pH of the purified ammophos suspension and the mass ratio of N: P_2O_5 are given in table. 4.

It should be noted that, on the one hand, the electrical conductivity of LCF is similar to known electrolytes, where with an increase in the pH and temperature of solutions, their density and viscosity decrease due to the destruction of the hydration shell and free movement of ions, on the other hand, an increase in the mass ratio of N: P_2O_5 leads to a decrease in the specific electrical conductivity , where, most likely, it is explained by the dissociation of ions with an increase in the amount of water (Table 4).

Table 4
Specific conductivity indices of liquid NP-fertilizers based on purified ammophos pulp and ammonium nitrate

Ratio of $N:P_2O_5$	Specific electrical conductivity, mS/cm (at temperatures, °C)						
	20	25	30	35	40	45	50
Ammophos suspension with pH value = 4.51							
1:0.5	49.08	54.67	60.26	65.86	71.36	76.73	80.16
1:0.7	43.23	49.35	55.45	61.54	67.14	71.91	75.82
1:1	37.38	44.04	50.64	57.21	62.92	67.10	71.47
Ammophos suspension with pH value = 5.53							
1 : 0.5	50.17	56.55	62.92	69.30	74.54	80.17	84.54
1 : 0.7	44.19	51.05	57.90	64.75	70.13	75.14	79.96
1:1	38.22	45.55	52.88	60.20	65.72	70.11	75.38
Ammophos suspension with pH value = 6.56							
1 : 0.5	52.38	59.14	65.90	72.66	78.39	84.86	89.30
1 : 0.7	46.14	53.39	60.64	67.89	73.76	79.54	84.46
1:1	39.90	47.64	55.38	63.12	69.12	74.21	79.62

The determination of vapor pressure over LCF was carried out by a dynamic method in the temperature range of 293-343 K. Constants A and B were calculated using the method of least squares using the Claisus-Cliperon equation and empirical equations were derived to determine the saturated vapor pressure over solutions.

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Table 5 shows the results of measuring the pressure of saturated vapors over the liquid liquid-liquid mixture solutions. The values of A and B, depending on the ratio of N: P_2O_5 and the pH of the pulp, range between 7.518-8.7439 and 1849-2271, respectively. It has been shown that the pressure of water vapor over the LCF decreases with an increase in temperature and salt mass of solutions.

Table 5

Vapor pressure of liquid balanced NP-fertilizers based on purified ammophos suspension (pH = 6.56) and ammonium nitrate

Ratio of N: P_2O_5	Equation type lgP=A-B/T	Vapor pressure, kPa (at temperatures, K)					
		293	303	313	323	333	343
1 : 0.5	lgP=7.518-1849/T	2.16	3.48	5.46	8.31	12.35	17.92
1 : 0.7	lgP=8.1172-2054/T	1.70	2.90	4.78	7.63	11.84	17.91
1 : 1	lgP=8.7439-2271/T	1.31	2.36	4.10	6.88	11.19	17.60

The given data confirm the low volatility of the HCS and their acceptability in the hot climate of Central Asia.

V. CONCLUSION AND FUTURE WORK

To increase the grade of LCF, that is, to obtain transparent suspensions, and to increase the water-soluble phosphorus in them, the process of separating the ammophos pulp into liquid and solid phases was carried out. At the same time, sediments containing high contents of total, assimilable and aqueous forms of phosphorus can be used as ammophos. And from the liquid phase - purified ammophos suspension, various brands of balanced liquid NP-fertilizers were obtained using the addition of ammonium nitrate. It is shown that the resulting NPK suspensions are in a fluid state. Their electrical conductivity is close to the electrical conductivity of known LCS. They have low volatility and can be stored for a long time without changing their physical and chemical properties.

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