

Microstructure of sodium tripolyphosphate obtained by spray-kiln method

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Introduction

Condensed phosphates are classified as inorganic polymers. There are three types of condensed phosphates: polyphosphates, cyclophosphates and ultraphosphates. Polyphosphates have a chain structure, ultraphosphates have a crosslinked structure. The degree of polymerisation ranges from 2 to 106 [1 ÷ 3]

One of the most important condensed sodium phosphates that are manufactured is sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$, STPP). It has been manufactured in bulk quantities since 1940 and it is used as component for detergents. The reason for the widespread use of STPP in detergents are its advantageous properties: ability to sequester calcium and magnesium ions in hard water, buffering capabilities, emulsion stabilising capability, deflocculating and dispersing properties [4,5].

Sodium tripolyphosphate (pentasodium triphosphate, STPP) exists in three crystalline forms. The stable form is the hexahydrate ($\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$). The other two polymorphic forms are anhydrous salts known as Phase I (high-temperature) and Phase II (low-temperature) [6 ÷ 8].

Phase I is formed at above 450°C, Phase II is formed at up to about 400°C. Manufactured STPP usually contains both these phases.

The anion of sodium tripolyphosphate consists of three condensed phosphate tetrahedrons. The P-O bonds in the anion form a broken line. The structure of the anion of Phase I, in comparison to that of Phase II, is characterized by higher deformation of terminal PO_4 groups and reverse internal symmetry of the molecule [8 ÷ 10].

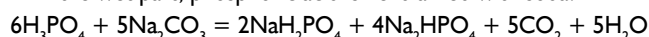
Both Phase I and Phase II crystallize in the monoclinic system. The principal difference between them is in the coordination of sodium ions [11 ÷ 13]. Two of the three independent sodium atoms in Phase I are coordinated by distorted oxygen tetrahedrons, with one of them positioned in the centre of inversion. The third sodium atom is surrounded by only four oxygen atoms.

In the crystallographic structure of Phase II, three sodium atoms are coordinated octahedrally by oxygen atoms.

Phase I, as compared to Phase II, is characterized by higher rate of hydration, which is the result of crystal structure distortion.

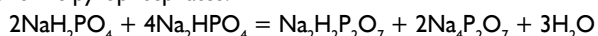
Sodium tripolyphosphate is manufactured commercially using either a one-step or a two-step method. Irrespective of the manufacturing method, sodium tripolyphosphate production comprises three chemical processes, and the production line includes a wet and a dry part [14].

In the wet part, phosphoric acid is neutralized with soda:

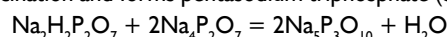


The molar ratio $\text{Na}_2\text{O} : \text{P}_2\text{O}_5$ (TM) in the neutralisation process is ca. 1.67. The product of this process is a mixture of orthophosphates, wherein there is 1 mole of sodium phosphate per 2 moles of disodium phosphate.

The dry part of the manufacturing plant includes drying and calcining systems. During drying the mixture of sodium phosphates is condensed and forms pyrophosphates:



The mixture of sodium pyrophosphates (disodium dihydrogen pyrophosphate and tetrasodium pyrophosphate) condenses during calcination and forms pentasodium triphosphate (STPP):



Drying and calcination conditions have an impact on the physicochemical properties of the product. Calcination temperatures determine the weight ratio of Phase I to Phase II in the final product [8, 9, 14].

This paper presents the results of investigations on the production of sodium tripolyphosphate, its physicochemical properties and on the effect of temperature on the morphology of calcination products.

Experimental

The starting material used in the tests was a mixture of sodium phosphates obtained in the spray drying process in an industrial STPP manufacturing plant.

In order to obtain sodium tripolyphosphate, the mixture of sodium phosphates was calcined in a chamber kiln for 60 minutes at 350 to 550°C.

The phase composition of the starting material and of the products was determined by X-ray radiography using a Philips X'Pert diffractometer with a graphite monochromator PW W 1752/00.

Thermal analyses of sodium phosphates was conducted on a SDT 2960 Simultaneous DTA-DTG thermal analyser from TA Instruments. Measurements were performed in air in the temperature range of 20 ÷ 800°C at a heating rate of 20°C/min.

Photographs of the grains were made using a Nikon Eclipse LV100 microscope. The material studied was also observed under a Hitachi S-4700 scanning electron microscope, which enabled the determination of material morphology. Samples were sputter-coated with Pd/Pt by means of a Cressington 208 HR sputter coater from Cressington Scientific Instruments Ltd.

Adsorption methods based on the plotting of gas adsorption/desorption isotherms were applied to determine specific surface area of the studied materials, pore volume and size distribution. Nitrogen adsorption/desorption measurements were made using ASAP 2405 apparatus from Micromeritics.

Density measurements were made using an AccuPyc 1330 helium pycnometer from Micromeritics. Bulk density was determined according to Polish standard

PN-80/C-04532 [15]. Pycnometric density of pelletized material was determined in a glass pycnometer. Kerosene was used as the liquid of known density, inert to samples. When the densities of the porous materials were known, their total and open porosity could be determined.

Discussion of results

It was found, on the basis of X-ray analysis, that the basic crystalline phase of the starting material used was a double salt of monosodium and disodium orthophosphates ($\text{NaH}_2\text{PO}_4 \cdot \text{Na}_2\text{HPO}_4$). The phases accompanying the double salt were disodium orthophosphate

(Na_2HPO_4), disodium orthophosphate dihydrate ($\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$), sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) and monosodium orthophosphate (NaH_2PO_4).

The result of thermal analysis of spray dried sodium phosphates, which enables determination of phase transitions that occur during the formation of sodium tripolyphosphate, is shown in Figure 1.

At ca. 73°C adsorbed water is released and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ is decomposed.

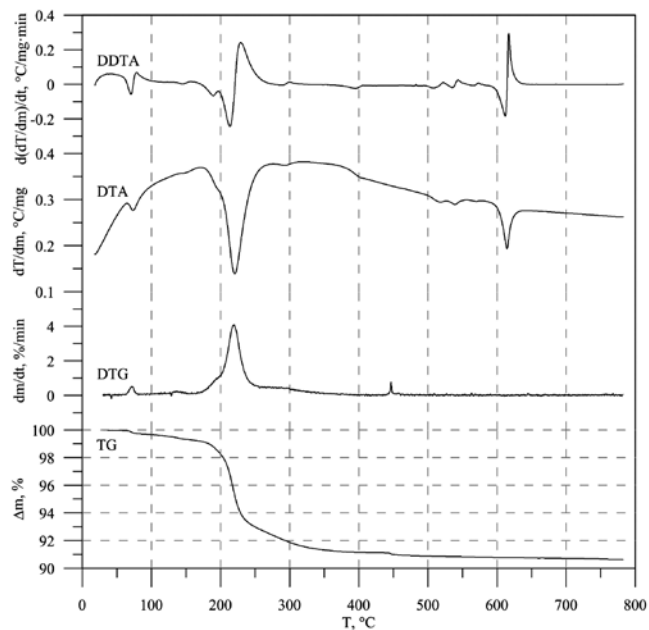


Fig. 1. Results of thermal analysis of sodium phosphates

Spray drying of the solution of sodium orthophosphates may lead to the formation of compounds of such disrupted structure, that they resemble amorphous substances. With increasing temperature during calcination (up to ca. 130°C) these compounds undergo recrystallisation.

In the temperature range of $180 \div 200^\circ\text{C}$ monosodium phosphate is converted into disodium dihydrogen pyrophosphate ($\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$). At the temperature of $200 \div 250^\circ\text{C}$ $\text{Na}_4\text{P}_2\text{O}_7$ is formed. At about 200°C anhydrous $\text{Na}_5\text{P}_3\text{O}_{10}$ is also formed. During further heating its rate of formation increases and reaches a maximum at ca. 290°C . At temperatures of up to 450°C the condensate structure takes on the form of Phase II. In the $450 \div 550^\circ\text{C}$ range Phase II is transformed into Phase I.

Transformations observed in the $360 \div 410^\circ\text{C}$ range are associated with the displacement of atoms due to diffusion in the solid body, leading to the synthesis of new compounds as the result of rearrangement of the starting material. At temperatures above 350°C low-molecular sodium metaphosphates (NaPO_3) start to form and are then transformed into higher molecular form ($\text{Na}_3\text{P}_3\text{O}_9$). The exothermic effect at ca. 480°C may be attributed to polymorphic transformation of the low-temperature phase of STPP into the high-temperature phase.

The three endothermic effects that occur in the DTA curve at $500 \div 590^\circ\text{C}$ are characteristic of the conditions of coexistence of solid and liquid phases. Under such conditions the solid phase melts in the liquid phase and the crystalline structure crumbles. Complete thermal decomposition of the crystalline phases coexisting in the product occurs at $600 \div 630^\circ\text{C}$.

Products obtained by calcining sodium phosphates for 60 minutes at $350 \div 550^\circ\text{C}$ were examined. X-ray radiography results have confirmed that the low-temperature STPP was the product of calcination at $350 \div 450^\circ\text{C}$. Phase transition of Phase II into Phase I commences at $450 \div 500^\circ\text{C}$. Product of calcination at 500°C is a mixture of both phases. Phase transition of Phase II into Phase I is completed at 550°C .

Table I lists the texture properties of the particles of the starting material and of the products determined by analysis of sorption isotherms. The table also includes the values of true density (d_t), bulk density (d_b) and pycnometric density (d_p). These values were used to determine the relative density (d_{rel}), total porosity (P_t) and open porosity (P_o) of the materials.

Table I

Parameters of microstructure of the starting material used and of calcinations products determined on the basis of densimetric and nitrogen sorption measurements

Parameter	Unit	Starting material	Product				
			350	400	450	500	550
Calcination temperature (T)	$^\circ\text{C}$	-	350	400	450	500	550
Bulk density (d_b)	g/cm^3	0.4053	0.4073	0.4300	0.4083	0.4163	0.4327
True density (d_t)		2.4828	2.6307	2.6226	2.6135	2.6065	2.5975
Pycnometric density (d_p)		1.2961	1.6354	1.6582	1.6655	1.7066	1.7201
Relative density (d_{rel})	%	16.32	15.48	16.40	15.62	15.97	16.66
Total porosity (P_t)	%	83.68	84.52	83.60	84.38	84.03	83.34
Open porosity (P_o)		68.73	75.09	74.07	75.48	75.61	74.84
Specific surface area (S_{BET})	m^2/g	0.99	0.63	0.75	0.57	0.55	0.48
External surface area (S_e)		1.84	1.08	1.65	1.22	1.16	0.79
Mesopore surface area (S_{meso})		1.17	0.76	0.99	0.75	0.68	0.55
Total pore volume (V_t)	cm^3/g	0.0022	0.0017	0.0017	0.0012	0.0011	0.0013
Mesopore volume (V_{meso})		0.0021	0.0017	0.0016	0.0011	0.0011	0.0012
Average pore diameter (D_{av})	nm	7.01	6.83	9.18	6.99	7.16	8.23
Mesopore diameter (D_{meso})		7.24	8.88	6.59	6.08	6.22	9.11

Figure 2 shows microscopic images of particles of the starting material and of product examples. Figure 3 shows SEM microphotographs of tested samples. The function of pore volume distribution vs. linear pore size is shown in Figure 4.

The high total porosity of sodium phosphates ($P_t = 83.68\%$), which translates into their low bulk density, is the result of specific morphology of particles. The grains of sodium phosphates have a spherical shape and characteristic "hollow shell" structure with wrinkled surface (Fig. 2). The examination of micro areas of the material shows that it is not uniform (grains vary in size and shape). The spray dried mixture has a form of polycrystalline aggregates. Diverse sizes and shapes also feature pores formed between the grains.

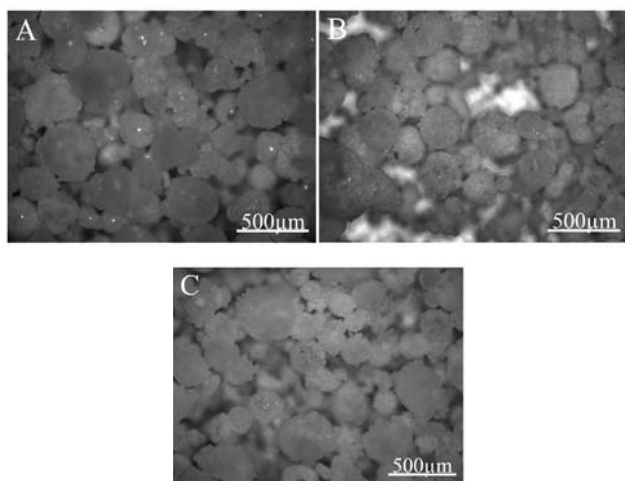


Fig. 2. Microscopic images of sodium phosphate particles after spray drying (A) and of sodium tripolyphosphate obtained at 350°C (B) and 550°C (C)

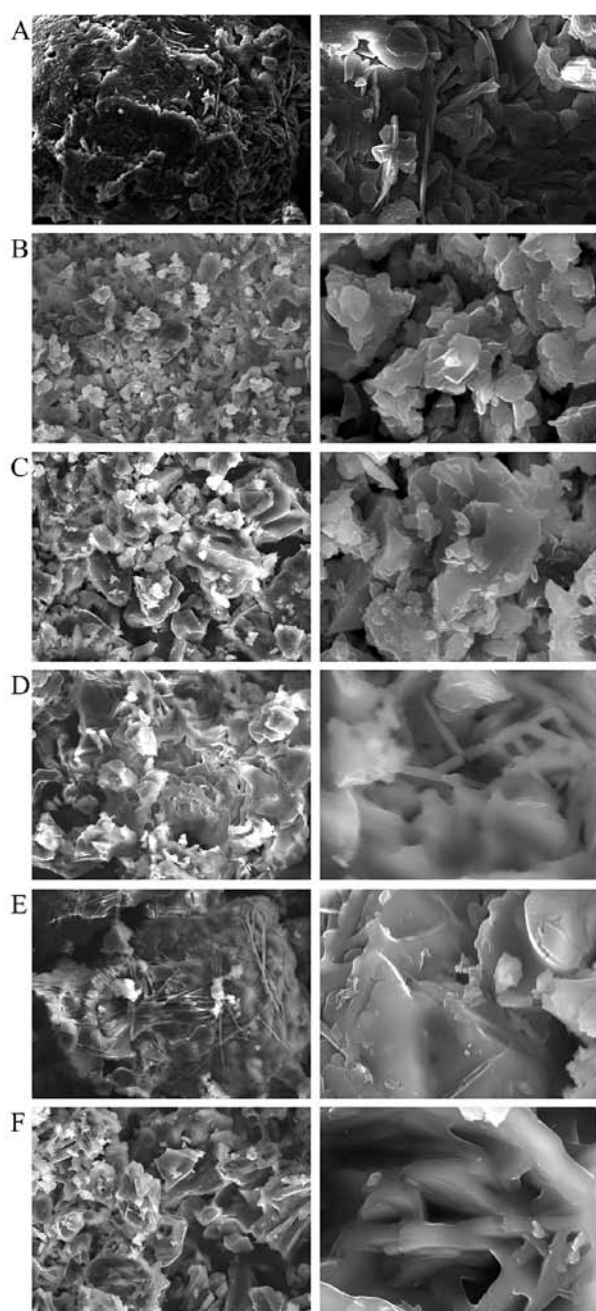


Fig. 3. SEM microphotographs of: A – starting material, B-F – products of calcination obtained at temperatures of 350, 400, 450, 500 and 550°C (magnification 1000x and 5000x)

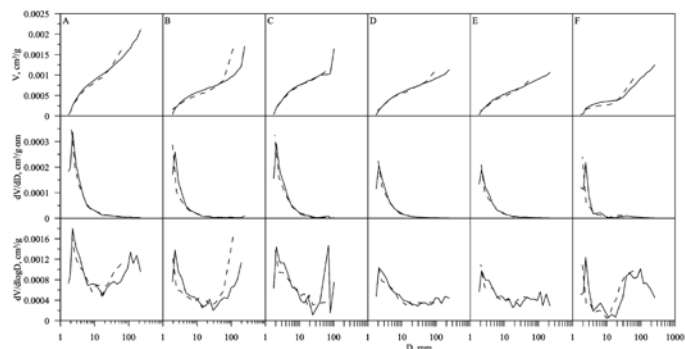


Fig. 4. Pore volume distribution vs. pore diameter in: A – starting material, B-F – products of calcination obtained at temperatures of 350, 400, 450, 500 and 550°C (solid line – adsorption; broken line – desorption)

Calcination preserves the structure of the starting material used. The presented microphotographs of STPP display the spherical structure of particles being the result of preserving the “hollow shell” structure of sodium phosphates after spray drying (Fig. 2). This is also confirmed by the high total and open porosities of this material (ca. 84% and 75%, respectively). The total and open porosities of the starting material are 84% and 70%, respectively.

Comparison of the images of the powder obtained at 350°C and those of sodium phosphate starting material (Fig. 3), indicates change of shape and size of the grains. The grains become partly more rounded and larger. The surface of contact between the grains also increases.

The result of microstructure changes is the decreasing of the specific surface area: from 0.99 m²/g of the sodium phosphates to 0.63 m²/g of sodium tripolyphosphate obtained at 350°C (Tab.1). The pore volumes and sizes are also contracted.

Material calcined at 400°C shows transitional loosening of the packing of grains and increased grain size. Pore volume distribution curves (Fig. 4) indicate substantial increase in mesoporosity. The logarithmic curve also indicates higher abundance of macropores. These changes cause increase in the development of the specific surface area of the material.

Specific in the microstructure of STPP obtained by calcination in 450°C and 500°C is the presence of oval and fibrous grains. Increased packing of grains, increased contact surface between grains and increased grain size are observed in the microstructure of material at 450°C and 500°C. The number and size of pores decrease, and the grains gradually form the solid skeleton of the material.

Sodium tripolyphosphate obtained at 550°C contains monocry-stalline grains with highly developed flat walls formed during liquid phase solidification. At this temperature of calcination the solid phase is partially transformed into liquid phase, which then resolidifies. The solidification of the liquid phase eliminates the smallest pores and decreases specific surface area. At the same time the process leads to the formation of a large number of macropores.

Conclusions

The phase composition of products depends on the calcination temperature. At 350÷450°C Phase II STPP is obtained, at 500°C a mixture of Phase II and Phase I, and at 550°C Phase I only.

The temperature of calcination also has an effect on the microstructure of sodium tripolyphosphate. At 350÷500°C the grains become more rounded and larger. After calcination at 550°C the grains have a fibrous form, the volume of the pores and the free surface area are increased. The change in morphology is the result of the presence of liquid phase at temperatures above 500°C. The liquid phase, present in the form of layers between solid grains, melts the grains. When the saturation concentration is exceeded, the solid phase reprecipitates from the liquid. This leads to decrease of pore volumes and denser packing of grains.

During the calcination of sodium phosphates the point of contacts between the grains are transformed into phase contacts with a higher surface development. Mass transfer within the porous set of grains into void spaces causes growth of grains and transformation of that set of grains into a solid polycrystal. Another effect of mass transfer is decrease of the free surface development and transformation thereof into grain boundaries. Small pores inside the spaces of dense grain arrangement are eliminated more rapidly than the wide pores between agglomerates. The result is breaking up of contacts between the grains, growth of pores and increased volumetric share of pores between agglomerates, and in consequence non-uniform microstructure. The processes of mass transfer are accompanied by a number of other phenomena, such as reactions between components or phase transitions, which can cause transitional changes in the microstructure.

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Bioplastics Award 2011: Call for Proposals Mönchengladbach, Germany, August 25, 2011

The trade publication bioplastics MAGAZINE is proud to present again the Bioplastics Award, one of the most recognized awards in the field of bioplastics. Suggestions for the 2011 Bioplastics Award can still be submitted to the judging panel. The 6th Bioplastics Awards will recognise innovation, success and achievement by manufacturers, processors and users of bioplastic materials. To be eligible for consideration in the awards the suggested company, product, or service must have been developed or on the market in 2010 or 2011.

Everybody can suggest an own product, service or development, or nominate their favourite example from another organisation. The organizers clearly encourage the global bioplastics community to participate. However, the winning company must send a representative to Berlin, Germany on 22/23 Nov. 2011 to receive the award. Details about the award can be found at www.bioplastic-smagazine.de/award. The entry should state: 1. Name and details of the company or person that should win the award 2. What the product, service or development is and does. 3. Why you think this product, service or development should win an award 4. What your (or the proposed) company or organisation does Each entry should not exceed 500 words (approx one page) and may also be supported with photographs, samples, marketing brochures and/or technical documentation. Completed entries shall be sent to award@bioplasticsmagazine.com. Winners will be announced on 22/23 Nov. 2011 during the 6th European Bioplastics Conference and published in the December issue of bioplastics MAGAZINE. Selection of the winner will be made by a panel of independent judges from Europe, America and Asia assembled by bioplastics MAGAZINE. The decision of the judging panel is final and binding. A pdf form for an award proposal can be found at www.bioplastic-smagazine.de/award

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