

chitin and chitosan as tobacco extenders will have to be determined by analyses of smoke components of chitin-tobacco cigarettes and biological testing of resulting smoke condensates.

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Received for review June 30, 1975. Accepted September 5, 1975. Reference to a company or product name does not imply approval or recommendation by the U.S. Department of Agriculture.

## Purification of Phosphoric Acid with Methanol and Ammonia

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In a laboratory study, wet-process phosphoric acid was lightly ammoniated and treated with methanol to precipitate most of the impurities as complex metal ammonium phosphates and fluorine compounds. The solids were separated and the methanol was distilled from the liquid phase for recycling. For rapid filtration and satisfactory purification of the acid, the initial mole ratio  $\text{NH}_3:\text{H}_3\text{PO}_4$  should be about 0.175 and the acid should be treated with about 2.5 lb of  $\text{CH}_3\text{OH}$  per lb of  $\text{H}_3\text{PO}_4$ . This treatment of the usual wet-process acid precipitated 90% or more of the Fe, Al, and F, up to 70% of the Mg, and 10% of the  $\text{P}_2\text{O}_5$ . The precipitate contained about 5% N and 50%  $\text{P}_2\text{O}_5$ , all of which was soluble in neutral ammonium citrate. Satisfactory filtration and settling required digestion of the methanol-acid mixture at 55°C or above for 30 to 50 min. The loss of methanol on distillation from 75%  $\text{H}_3\text{PO}_4$  could be kept below 50 lb per ton of  $\text{P}_2\text{O}_5$ , but there was some esterification to form monomethyl phosphate. This esterification increased with rising temperature of distillation and with increasing concentration of acid. It was minimized by distillation under vacuum and was negligible when the initial acid was only moderately concentrated.

Wet-process phosphoric acid contains metallic and fluorine impurities that form troublesome precipitates when the acid is converted to solution fertilizers (Frazier et al., 1972). Various purification processes have been developed to upgrade the acid to food, detergent, or solution fertilizer quality (Blumberg, 1971). Most of the processes are based on solvent extraction methods which divide the acid into purified and raffinate fractions. The methanol process is based on precipitation of impurities from lightly ammoniated wet-process phosphoric acid with methanol to produce acid suitable for solution fertilizer production.

Methanol alone does not precipitate impurities from the acid, but when alkali or ammonium ions are also present, most of the impurities are precipitated as complex alkali or ammonium metallic phosphates and fluorine compounds (Pulverfabrik Skodawerke-Wetzler A.-G., 1937). Alkali or ammonium ions can be added as any soluble source. Anhydrous ammonia was used in this study because no contaminating anions are thus introduced, and the nitrogen is recovered in the final fertilizer products. Other acid-miscible solvents also can be used (Pulverfabrik Skodawerke-Wetzler A.-G., 1937; Frankenfeld and

Götzmann, 1973; British Patent, 1974). Methanol, however, has the advantage of being cheaper than other potential solvents.

The methanol process consists of the following basic steps: recycled methanol, ammonia, and wet-process acid are brought together in a reactor to precipitate the impurities; precipitated impurities are separated from the methanol-acid mixture; and methanol and part of the water are distilled from the purified acid and separated in a fractionating column. Except for rectification, each of the steps was investigated in the laboratory for the purification of merchant-grade phosphoric acid. Esterification and ether formation during distillation also were investigated.

## ANALYTICAL METHODS

Standard analytical procedures were used for determination of  $\text{P}_2\text{O}_5$  and nitrogen (Association of Official Analytical Chemists, 1970). Low results for phosphorus were obtained when monomethyl phosphoric acid was present, presumably because the ester was not decomposed in the boiling  $\text{HNO}_3$  solution normally used for digestion of the sample. Correct results were obtained by heating the sample with  $\text{H}_2\text{SO}_4$  to fumes and then adding  $\text{HNO}_3$  dropwise to oxidize the organic matter.

All metals were determined by atomic absorption spectrophotometry (Perkin-Elmer, 1971). Fluorine was

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Table I. Composition of Wet-Process Phosphoric Acids

No.	P <sub>2</sub> O <sub>5</sub> content, wt %	Impurities, g/kg of P <sub>2</sub> O <sub>5</sub>				Wt ratio F:Mg
		Fe	Al	Mg	F	
Black Acids <sup>a</sup>						
1	54.1	20.3	13.3	3.33	16.6	5.00
2	54.4	25.7	9.93	4.04	14.7	3.64
3	54.6	16.7	16.5	6.95	16.5	2.37
4	54.0	13.3	18.5	10.2	18.5	1.82
Green Acids <sup>b</sup>						
5	52.8	19.7	7.20	11.6	11.6	1.00
6 <sup>a</sup>	54.2	12.9	8.86	5.16	3.32	0.64
7	53.0	15.8	7.00	2.08	5.85	2.81
Mixed Black and Green Acid <sup>c</sup>						
8	53.6	20.1	10.8	6.52	14.6	2.23

<sup>a</sup> Made from uncalcined phosphate rocks. <sup>b</sup> Made from calcined phosphate rocks. <sup>c</sup> 60% acid no. 1 and 40% acid no. 5.

determined by titration with thorium nitrate after it was distilled from acid solution. When methanol was present it was removed by evaporation of the alkalinized sample.

Phosphate esters in the distillation residues were determined by ascending paper chromatography with a solvent consisting of 70% by volume of 1-propanol and 30% of 2 N NH<sub>4</sub>OH (Moule and Greenfield, 1963). Chromatograms were eluted for 20 hr at ambient temperature on S&S No. 589 orange ribbon paper cut to the standard wick configuration. The chromatograms were developed under ultraviolet light after being sprayed with an ammonium molybdate-perchloric acid solution (Karl-Kroupa, 1956). The *R<sub>f</sub>* values for orthophosphate and monomethyl and dimethyl phosphate were 0.26, 0.31, and 0.64, respectively. The results of tests of the reproducibility of the method showed an average absolute error of ±0.3%.

Methanol and water in the distillates were determined by gas chromatography. Distillate components were separated with a gas chromatograph fitted with a 10 ft length of 0.25-in. stainless steel tubing packed with 50–80 mesh Poropak-Q. Helium was passed through the column at a rate of 60 cm<sup>3</sup>/min. Water and methanol were determined with the column at 100°C and calculated from the peak height ratio H<sub>2</sub>O:CH<sub>3</sub>OH, and a standard curve was obtained by plotting the ratios against the water content of standard CH<sub>3</sub>OH–H<sub>2</sub>O solutions. The average absolute error in the standard curve was ±0.3% H<sub>2</sub>O. Dimethyl ether was separated at 70°C, but the amount in the distillate was too low for quantitative determination.

#### BATCHWISE PRECIPITATION

The batchwise precipitation of impurities was studied over a wide range of ratios of N:P and of CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> to determine the effects of the ratios on purification and recovery of acid. A black acid (no. 1, Table I) prepared from Florida rock and a green acid (no. 5, Table I) prepared from calcined North Carolina rock were used in the tests. Other than their carbon contents, the most significant difference between the acids was their magnesium contents.

The precipitations were made in a 1-l., three-necked flask equipped with reflux condenser, magnetic stirrer, thermometer, and ammonia sparger. One mole of H<sub>3</sub>PO<sub>4</sub> was sparged with the calculated amount of ammonia and then methanol was dripped into the stirred acid. The resulting slurry was refluxed for 30 min at 68 to 70°C, then cooled to 30°C, and filtered by suction; the cakes were washed with 200 ml of methanol. Filtrates from black acid

Table II. Composition of Methanol Precipitates<sup>a</sup>

Mole ratio N:P	Composition, wt %					
	P <sub>2</sub> O <sub>5</sub>	N	Fe	Al	Mg	F
0.05	40.6	3.5	6.1	7.6	2.0	10.8
0.10	45.9	4.4	7.4	5.4	1.0	6.0
0.14	46.7	4.8	6.8	4.9	1.0	5.3
0.15	47.2	5.3	6.7	4.8	1.0	4.8
0.16	49.6	5.6	5.3	3.9	0.8	3.5
0.20	50.1	6.3	5.5	3.9	0.8	4.2

<sup>a</sup> Weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 6.9.

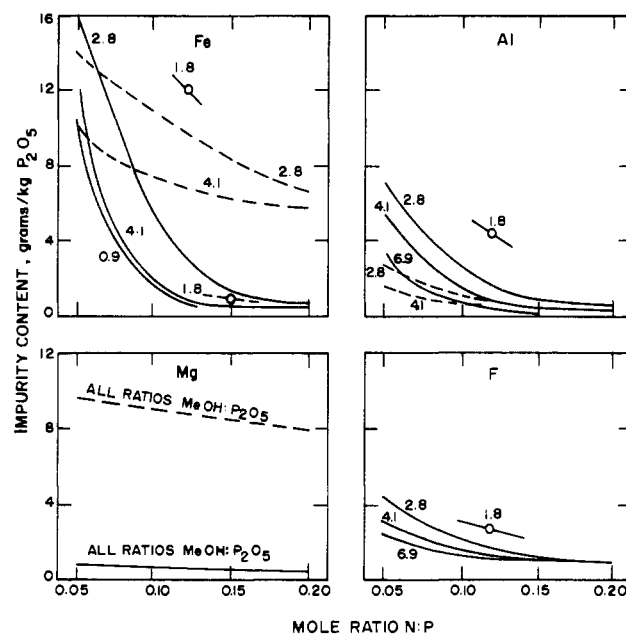


Figure 1. Impurity contents of methanol extracts. (Numbers on curves are weight ratios MeOH:P<sub>2</sub>O<sub>5</sub>; solid lines refer to acid no. 1; dashed lines refer to acid no. 5.)

were dark in color because none of the carbon was removed.

The filter cakes, when dried at 62°C, were fine-grained and easily pulverized to off-white powders with low bulk densities. When the free acid was completely removed, the cakes had a neutral reaction. Examination by x ray showed that they were amorphous except for small amounts of NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> present in cakes precipitated with the larger amounts of methanol and ammonia. The compositions of filter cakes obtained from the black acid at different ratios N:P and with weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 6.9 are shown in Table II. They contained up to 50% P<sub>2</sub>O<sub>5</sub> and up to 6% N; all the P<sub>2</sub>O<sub>5</sub> was available and about 50% was water soluble by official AOAC procedures.

The purification results are summarized in Table III, and the impurity levels of the treated acids are plotted in Figure 1 as functions of mole ratio N:P. In these tests the ammoniation mole ratio N:P ranged from 0.05 to 0.2, and the weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> was from 1.8 to 6.9. The larger amounts of methanol removed more Fe, Al, and F from the black acid at the lower ammoniation levels, but the differences decreased with an increase in ammoniation and were negligible at mole ratio N:P of about 0.15. The effect of methanol on the removal of Al and F from the green acid was similar to that on the black acid, but the largest amount of methanol was required to remove most of the iron at the higher ammoniation levels. With both acids, the amount of methanol had little effect on the removal of Mg.

Except for the removal of Mg from the black acid, the removal of impurities generally increased with an increase

Table III. Batchwise Purification of Wet-Process Acids

Acid no.	Wt ratio MeOH:P <sub>2</sub> O <sub>5</sub>	Mole ratio N:P	Composition of precipitate, %		Filtrate						
			P <sub>2</sub> O <sub>5</sub>	N	Recovery, %		Impurities, g/kg of P <sub>2</sub> O <sub>5</sub>				
					P <sub>2</sub> O <sub>5</sub>	N	N	Fe	Al	Mg	F
1	1.8	0.12	41.2	4.1	95	77	19	12	4.4	0.73	2.7
1	2.8	0.05	33.1	2.8	98	81	8.0	16	7.0	0.72	4.4
		0.10	44.3	4.4	92	61	13	6.1	2.6	0.61	2.3
		0.11	45.8	4.6	91	59	14	2.9	2.2	0.61	2.0
		0.14	47.0	4.9	89	60	19	0.80	0.8	0.5	1.4
		0.16	47.1	5.0	88	60	21	1.1	0.8	0.5	2.1
		0.19	46.8	5.6	89	64	28	0.80	0.5	0.5	1.1
		0.20	47.2	5.5	88	64	29	0.6	0.3	0.5	1.1
1	4.1	0.05	38.2	3.3	96	67	7.0	12	5.2	0.7	3.2
		0.11	47.1	4.5	91	59	14	1.1	1.1	0.6	1.5
		0.15	48.0	5.0	88	57	19	0.20	0.2	0.3	1.4
		0.19	48.8	5.7	85	55	25	0.50	0.3	0.5	1.0
1	6.9	0.05	40.6	3.5	95	58	6	10.4	3.6	0.74	2.5
		0.10	45.9	4.4	90	50	11	0.89	0.50	0.92	1.5
		0.14	46.7	4.8	88	44	18	0.5	0.2	0.64	1.1
		0.15	47.2	5.3	88	53	18	0.2	0.2	0.8	1.3
		0.16	49.6	5.6	84	44	17	0.2	0.2	0.6	1.1
		0.20	50.1	6.3	84	47	20	0.3	0.2	0.5	1.0
5	2.8	0.05	39.4	2.9	97	79	8	14	3.0	9.5	2.9
		0.11	45.5	4.4	94	69	15	9.5	1.1	9.2	2.6
		0.16	44.8	5.0	93	76	24	8.7	0.6	8.6	1.0
		0.20	45.9	5.6	92	75	33	6.4	0.3	8.2	1.0
5	4.1	0.05	43.8	3.5	95	62	7	10	1.6	9.5	2.9
		0.10	45.7	4.5	93	65	15	7.4	0.8	9.1	3.3
		0.16	46.3	5.2	91	69	24	6.0	0.3	8.4	1.6
		0.20	46.3	5.3	91	73	32	5.9	0.2	7.9	0.8
5	6.9	0.16	47.0	5.2	90	65	24	0.92	0.2	8.3	0.8
2	4.1	0.16	49.7	4.7	86	58	21	0.5	0.3	1.8	1.3
3	4.1	0.15	48.5	5.1	86	55	18	0.8	1.2	3.4	0.7
4	4.1	0.15	46.6	5.7	88	50	18	2.2	0.8	5.8	1.1
6	4.1	0.15	52.4	5.4	90	66	22	1.0	0.9	4.4	0.2
8	4.1	0.10	44.9	4.5	91	55	12	3.2	1.0	3.8	1.6

in mole ratio N:P up to about 0.15. Maximum purification of the black acid with a minimum amount of methanol was obtained with mole ratio N:P of 0.15 and weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 2.8, whereas maximum purification of the green acid at this ratio N:P occurred with weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 6.7. Under the same conditions Al and F were removed from both acids with equal effectiveness, but smaller fractions of Fe, and particularly of Mg, were removed from the green acid than from the black acid. When ammoniated to mole ratio N:P of 0.15 and treated with 2.8 parts of methanol per part of P<sub>2</sub>O<sub>5</sub>, both types of acid retained 1 to 2 g of F and less than 1 g of Al per kg of P<sub>2</sub>O<sub>5</sub>. Under these conditions the green acid retained about 8 g each of Fe and Mg per kg of P<sub>2</sub>O<sub>5</sub>, as compared with less than 1 g each of Fe and Mg per kg of P<sub>2</sub>O<sub>5</sub> retained by the black acid.

Because there were such marked differences between the precipitation of Mg from the black acid and from the green acid and because the ratio F:Mg in the black acid was 5 times that in the green acid, tests were made in which the ratio in the acids was varied by the addition of NH<sub>4</sub>HF<sub>2</sub> or Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. The results (Figure 2) showed that the fraction of Mg precipitated increased with increasing ratios of F:Mg and indicated that Mg is precipitated as a fluorine compound. Low ratios of F:Mg usually reflect high magnesium contents, and thus it appears that some purified acids will retain relatively high amounts of Mg.

Additional tests were made with five other acids including a green acid. The results (Table III) were consistent with those from acids no's. 1 and 5, except that Fe was removed as effectively from the green acid as from the black acid. It is not clear why green acid no. 5 behaved so differently from other acids with respect to precipitation of Fe. Of the ten different acids (including three green acids) tested in the complete study, green acid no. 5 was

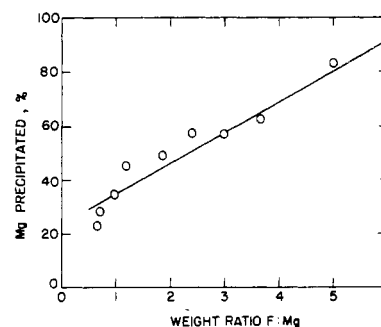


Figure 2. Effect of ratio F:Mg on removal of magnesium.

the only one that behaved anomalously.

The recovery of phosphate as purified acid naturally depends primarily on the degree of purification and on the amount of impurities in the raw acid. In addition, high ammoniation and methanol levels cause precipitation of some NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. With weight ratios CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 2.8 to 4.1 and mole ratio N:P of 0.15, where 90% or more of the impurities are precipitated, 86 to 89% of the phosphate in the black acid was recovered and 91 to 93% of the phosphate in green acid no. 5 was recovered.

#### CONTINUOUS PRECIPITATION

In a further study of the process, the impurities were precipitated under continuous conditions in laboratory equipment. A preliminary study with three black acids prepared from Florida rock indicated that the optimum conditions for maximum purification with good filtration were mole ratio N:P of about 0.175, weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of about 3.9, a temperature of 50°C or higher, and about 50 min retention time. Acids purified under these conditions contained less than 2 g each of Fe, Al, Mg, and F per kg of P<sub>2</sub>O<sub>5</sub> which corresponded to the

Table IV. Continuous Purification of Wet-Process Acids

Run no.	Wt ratio CH <sub>3</sub> OH:P <sub>2</sub> O <sub>5</sub>	Purified acid													
		Fraction, %, of total recovered			Composition, g/kg of P <sub>2</sub> O <sub>5</sub>					Composition, %, of precipitate					
		P <sub>2</sub> O <sub>5</sub>	N		N	Fe	Al	Mg	F	P <sub>2</sub> O <sub>5</sub>	N	Fe	Al	Mg	F
Mole Ratio N:P = 0.153															
1	2.80	91.1	73	24	3.0	1.3	1.3	1.3	53.4	4.9	7.6	3.8	0.29	1.8	
2	3.23	91.6	70	23	1.2	0.8	1.4	1.2	52.0	5.1	8.1	4.0	0.37	2.2	
3	3.71	90.5	72	24	2.6	0.9	1.3	1.3	53.5	5.0	7.8	3.6	0.36	1.1	
4	4.48	89.7	71	24	0.9	0.3	1.2	1.6	54.2	4.7	7.6	3.8	0.42	1.5	
Mole Ratio N:P = 0.178															
5	2.94	90.4	75	29	1.5	0.6	1.4	1.7	53.6	5.1	7.7	3.9	0.46	2.0	
6	3.22	90.6	72	28	0.8	0.5	1.4	1.5	52.0	5.4	7.8	3.7	0.41	2.1	
7	3.73	89.5	74	29	1.0	0.4	1.3	1.2	54.0	5.1	7.4	3.6	0.50	1.9	
8	4.46	90.0	76	30	0.7	0.2	0.8	1.3	52.5	5.4	7.7	3.9	0.54	1.9	
Mole Ratio N:P = 0.201															
9	2.91	90.4	74	32	1.0	0.5	1.2	1.4	52.4	5.4	7.7	3.8	0.50	2.2	
10	3.23	89.4	72	32	0.9	0.4	1.1	1.2	53.5	5.3	7.7	3.7	0.49	1.4	
11	3.71	90.4	74	32	1.0	0.3	1.0	1.0	51.4	5.8	8.0	3.8	0.60	2.7	
12	4.43	90.8	73	32	0.6	0.2	0.9	1.1	50.4	5.8	8.2	4.3	0.62	2.7	

removal of 90% or more of the Fe, Al, and F and 50 to 70% of the Mg from the raw acid. Filtration rates of 200 gal/(hr ft<sup>2</sup>) or more were obtained.

A more detailed study was then made with a green acid prepared from calcined Florida rock (no. 7, Table I). Runs were made at 60°C and 50 min retention time at each of the 12 combinations of mole ratios N:P of 0.153, 0.179, and 0.201, and weight ratios CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 2.9, 3.2, 3.7, and 4.6.

The reactor was a thermostated 500-ml, three-necked flask equipped with feed tubes, an outlet tube, and a sealed stirrer. When operating, the reactor held about 300 ml of slurry which overflowed the reactor to a 1-l. three-necked round-bottomed flask that served as a digester and a sample collector. The flask was thermostated at the same temperature as the reactor and was fitted with a sealed stirrer, reflux condenser, and a sample discharge tube. The flask could be isolated from the reactor and pressurized to completely eject the slurry.

Preammoniated acid (1.7 to 2.5 ml/min) and methanol (7 to 9 ml/min) were accurately metered ( $\pm 1\%$ ) with a displacement feeder. Acid was ammoniated with reagent NH<sub>4</sub>HCO<sub>3</sub>, and water was added as needed to maintain the ratio H<sub>2</sub>O:P<sub>2</sub>O<sub>5</sub> constant. Runs were begun with the reactor filled with a digested slurry of the correct composition, and the product was discarded for 2.3 retention times to discharge 90% of the starting slurry. The system then was considered to be near steady state, and samples were taken every 40 min for the next 8 hr. Filtration tests were made on each sample and portions from every other sample were taken for sedimentation tests and analysis. All the slurry in the digester (about 400 ml) was ejected every 40 min and used in filtration and other tests. The average retention time in the digester thus was 20 min, and this time was added to the retention time in the reactor to give a total retention time of 50 min.

Analytical samples (50 g) were weighed, filtered, and washed with 100 ml of methanol. Sedimentation data were obtained by recording settled volumes at intervals in a 50-ml graduate. Filtration and washing tests were made with about 300 g of sample and 200 ml of methanol on a 4.52-in.<sup>2</sup> heated filter at 15 in. of Hg. The filtering medium was 400-mesh Saran cloth. Filter cakes were allowed to drain for 10 sec, after which they were weighed and dried to constant weight.

Purification data are shown in Table IV and are reported as the average of the last four or five samples taken at steady-state conditions. The amount of impurities re-

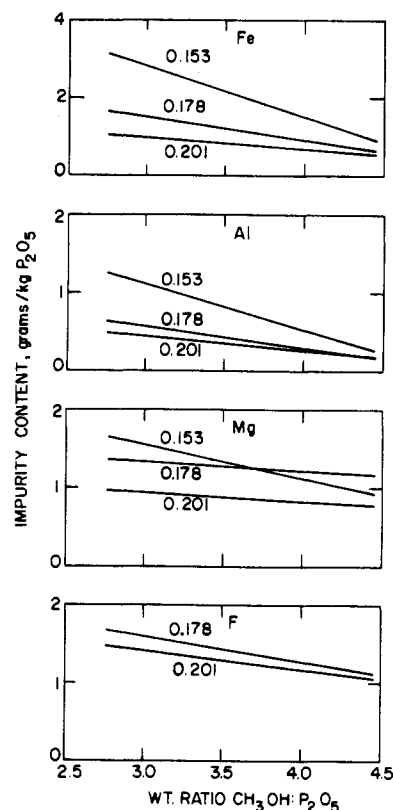


Figure 3. Effect of methanol content on impurities remaining with purified acid at different mole ratios N:P. (Numbers on curves denote ratio of N:P.)

maining with the treated acid generally decreased with increasing levels of ammoniation and methanol (plotted as smoothed curves in Figure 3). At mole ratio N:P of 0.178 and all ratios of CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub>, the amounts of impurities per kg of P<sub>2</sub>O<sub>5</sub> in the treated acid were less than 1.6 g of Fe, 0.7 g of Al, 1.4 g of Mg, and 1.7 g of F. The fraction of F, and especially of Mg, removed from the acid was lower than that obtained with other acids having comparable ratios of F:Mg. However, the raw acid was unusually low in both fluorine (0.31%) and Mg (0.11%).

Over the range tested, the amounts of methanol and ammonia had little effect on recovery of P<sub>2</sub>O<sub>5</sub> as purified acid. The overall average was 90.4  $\pm$  0.9%. The filter cakes contained 50 to 54% P<sub>2</sub>O<sub>5</sub>, which is higher than that obtained with other acids. This is attributed to the low

Table V. Filtration of Acid-Methanol Slurries

Run no.	Wt ratio CH <sub>3</sub> OH:P <sub>2</sub> O <sub>5</sub>	Slurry		Filtration			
		Density at 60°C, g/ml	Wt % solids	Rate, gal/(hr ft <sup>2</sup> )		Volatiles in wet cake, %	Cake thickness, cm
				Slurry	Wash		
				Mole Ratio N:P = 0.153			
1	2.86	0.982	3.4	470	402	48	1.1
2	3.22	0.966	3.1	440	320	46	0.9
3	3.71	0.942	3.2	260	210	58	1.2
4	4.48	0.915	3.0	160	150	67	1.4
				Mole Ratio N:P = 0.178			
5	2.94	0.980	3.8	280	220	57	1.5
6	3.22	0.964	3.5	220	200	57	1.3
7	3.73	0.942	3.5	110	120	65	1.6
8	4.46	0.915	3.0	62	64	73	1.6
				Mole Ratio N:P = 0.201			
9	2.91	0.981	3.8	210	190	57	1.4
10	3.22	0.966	3.9	110	140	62	1.6
11	3.71	0.941	3.2	46	57	67	
12	4.43	0.913	2.8	21	22	72	

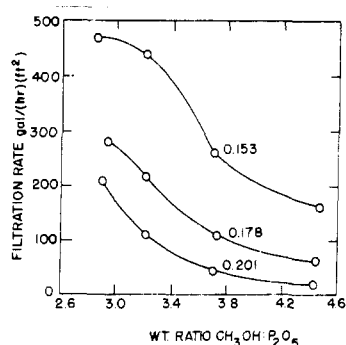


Figure 4. Effect of methanol on rate of filtration at different mole ratios of N:P. (Numbers on curves denote ratio of N:P.)

F and Mg contents resulting from the unusually low contents of these impurities in the raw acids. As in products from batch precipitation, all the P<sub>2</sub>O<sub>5</sub> in the precipitates was available and about 50% was water soluble. A composite sample of the precipitates tested in the greenhouse as a phosphorus source for corn was only slightly less effective than conventional phosphate sources.

Results from filtration and washing tests are shown in Table V along with other data. Filtration and washing rates are reported as the average of six to eight tests from each run after steady state was reached. All standard errors in the measurements were less than 10%; the average value was 4%. The filtration rates decreased with increasing ammonia and methanol concentrations (Figure 4). The rate of filtration ranged from 470 gal/(hr ft<sup>2</sup>) with the smallest amounts of CH<sub>3</sub>OH and NH<sub>3</sub> to 20 gal/(hr ft<sup>2</sup>) with the largest amounts of CH<sub>3</sub>OH and NH<sub>3</sub>. Washing rates were lower than filtration rates at the lower concentrations of methanol and were about the same at the higher concentrations of methanol.

Smoothed sedimentation curves from runs made at mole ratio N:P of 0.178 and different amounts of CH<sub>3</sub>OH are plotted in Figure 5. Results from three to five samples from each run taken at steady state are included in each curve. As expected, settling rates paralleled filtration rates; slurries that filtered rapidly also settled rapidly. The rapid settling of slurry prepared at mole ratio N:P of 0.178 or less and at weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 3.7 or less suggests that in a process it might be economical to include a thickening step to decrease the volume of slurry to be filtered.

The results from these studies indicate that the continuous process can be operated under conditions to

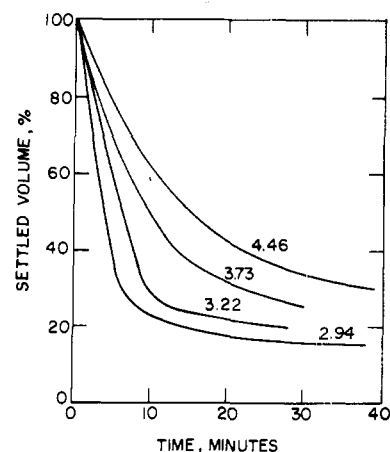


Figure 5. Settling curves at mole ratio N:P of 0.178. (Numbers on curves denote weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub>.)

produce slurry that filters and settles extremely fast, but these conditions do not give the best purification. These conditions will, however, remove more than 80% of the Fe, Al, and F and more than 50% of the Mg from most wet-process acids. If medium filtration rates of about 150 gal/(hr ft<sup>2</sup>) are acceptable, better purification is obtained. When the process was operated at mole ratio N:P of 0.178 and at weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 3.50, conditions which gave a filtration rate of 150 gal/(hr ft<sup>2</sup>), the grams of impurities per kg of P<sub>2</sub>O<sub>5</sub> left with the purified green acid were: N, 28; Fe, 1.2; Al, 0.45; Mg, 1.3; and F, 1.4.

#### RECOVERY OF METHANOL

The distillation phase of the process was studied in simple batch distillations of methanol from phosphoric acid at different concentrations, temperatures, and pressures. Mixtures of known concentration (1100–1400 g) were distilled from a 2-l. flask equipped with a magnetic stirrer, thermometer, and heating mantle. Vapors were condensed in a primary condenser at 15°C and in a secondary condenser at -15 to -20°C. The condensers were surmounted by a -50°C cold trap. Reduced pressures were maintained by a vacuum pump and measured with a mercury manometer. In some tests distillate was caught in a receiver located above the distillation flask so that distillate could be returned to the acid through a stopcock. Distillations were made as rapidly as practicable to minimize the time at high temperature. When the desired temperature was reached, heating was discontinued and the distillation flask was cooled by a stream of compressed air. The distillate,

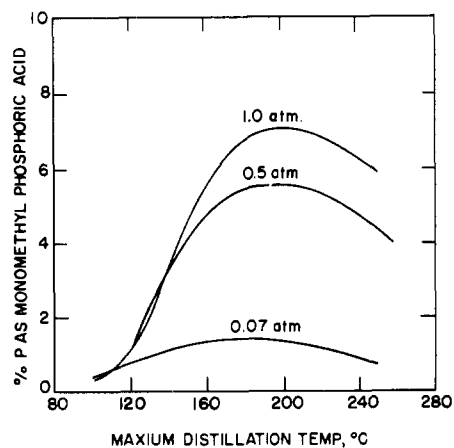


Figure 6. Effect of temperature on ester formation.

residue, and cold-trap condensate were weighed and analyzed. Typically, about 99.7% of the input weight was recovered; the rest was mostly material retained by the apparatus.

In initial tests of the stability of methanol on distillation from  $H_3PO_4$ , methanol was distilled at atmospheric pressure from 74.6% reagent  $H_3PO_4$  (weight ratio  $CH_3OH:P_2O_5$  of 4.1) until the temperature rose to 160°C. The distillate was returned to the acid and redistilled. This process was repeated 10 times to allow the reaction products to accumulate and to distribute mechanical losses among the different distillations. After ten cycles the residue was clear amber in color and contained 4.4% carbon. Analysis by pH titration (McCullough, 1973) and by paper chromatography showed that most of the carbon was present as monomethylphosphoric acid (no other ester was detected) and that about 38% of the phosphorus was esterified.

The cold trap contained a volatile liquid that was identified as dimethyl ether by infrared spectrophotometry. The amount of ether was equivalent to about 3% of the input methanol. The ether probably was produced from the ester by reactions analogous to those of sulfuric acid and alcohols.

The gas chromatogram of the distillate showed only three peaks corresponding to water, methanol, and traces of dimethyl ether. The distillate contained 92% of the input alcohol, which indicated a methanol loss of 73 lb/ton of  $P_2O_5$ /distillation.

Single distillations of methanol from reagent  $H_3PO_4$  were made to determine the effects of temperature, pressure, and concentration on esterification, ether formation, and recovery of methanol. In some of these tests, the distillations were stopped at different preselected temperatures, and in other tests the distillations were continued to a temperature of 200°C. The experimental conditions and results are shown in Table VI.

Little or no ether was condensed in the cold trap, but gas chromatography showed traces of ether in distillates produced at temperatures above 140°C and at pressures of 0.5 atm and above. The largest amount of ether in the distillates was less than 0.05% and was found in distillate produced at 1 atm and 250°C. No ether was detected in distillate produced at 0.07 atm, but this may have resulted in part from the difficulty of condensing ether in the high vacuum. Much less ether was formed in the single distillations than was formed in each distillation in the recycle tests. This is attributed to the lower ester concentrations and to the shorter exposure to high temperature. Although the ether formed in the single distillations is negligible when considered as alcohol loss, even trace amounts could

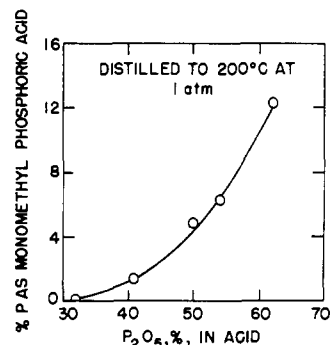


Figure 7. Effect of acid concentration on esterification.

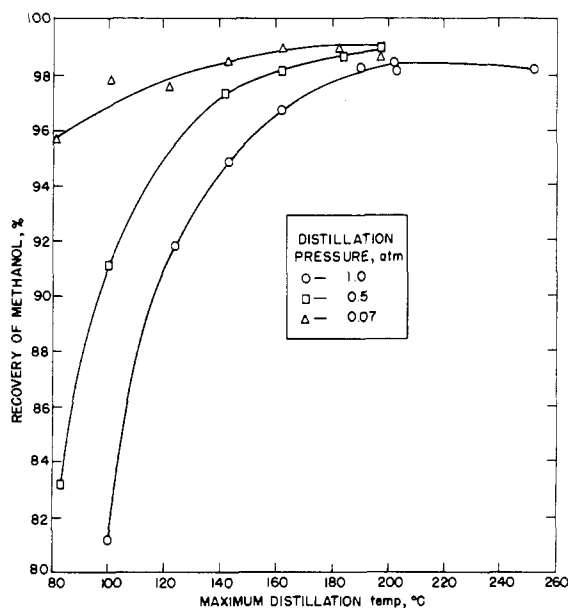


Figure 8. Effect of temperature on recovery of methanol.

cause problems in an industrial process.

Esterification is first detectable at about 100°C and then increases with rising temperature until maxima are reached at temperatures from 170 to 200°C (Figure 6). The presence of maxima shows that the ester begins to decompose at the higher temperatures. Esterification is decreased by distillation at reduced pressure. At 0.07 atm, the maximum amount of esterification was about 1.5% as compared with a maximum of about 7% in distillation at 1 atm (Figure 6).

Esterification increases with an increase in acid concentration (Figure 7). Distillation of methanol from 62%  $P_2O_5$  reagent acid to a temperature of 200°C resulted in the esterification of 12.5% of the acid, but no esterification was detected with acid containing 32%  $P_2O_5$ . Other data in Table VI show that esterification increases with an increase in the ratio  $CH_3OH:P_2O_5$ , especially at higher acid concentrations. This would be expected because of the mass action effect and, more importantly, because of the greater dewatering effect.

The recovery of methanol as distillate is plotted in Figure 8 as a function of maximum distillation temperature for the distillation of methanol from 54%  $P_2O_5$  reagent acid (weight ratio  $CH_3OH:P_2O_5$  of 2.76). The plots indicate that temperatures near 200°C are required for maximum recovery of methanol in simple batch distillation. At 0.07 atm, however, the increase in methanol recovery at temperatures above 160°C was slight and well within the experimental error. At temperatures of 200°C, and within the experimental error of 0.5 to 1.0%, all the methanol was

Table VI. Distillation of Methanol from Phosphoric Acid

No.	Max. distln. temp., °C	Acid concn, % P <sub>2</sub> O <sub>5</sub>	Wt ratio CH <sub>3</sub> OH:P <sub>2</sub> O <sub>5</sub>	Residue			Distillate composition, %			Total wt acct. for	CH <sub>3</sub> OH, % of input		
				Total P <sub>2</sub> O <sub>5</sub> , %	% P as		CH <sub>3</sub> OH	H <sub>2</sub> O	Ether		Distl.	Ester	Unac-counted for <sup>a</sup>
1 atm													
1	100	54.0	2.76	46.3	0.8	99.2	91.7	8.3	0	99.84	81.2	0.1	18.7
2	123	54.0	2.76	55.7	1.6	97.7	90.2	9.8	0	99.79	91.8	0.3	7.9
3	142	54.0	2.76	60.0	3.3	95.9	89.2	10.8	tr	99.81	94.9	0.5	4.6
4	161	54.0	2.76	63.2	6.5	93.1	88.4	11.6	tr	99.83	96.8	1.1	2.1
5	189	54.0	2.76	67.1	6.8	93.0	87.2	12.8	tr	99.81	98.3	1.1	0.6
6	201	54.0	2.76	68.0	6.1	93.3	86.9	13.1	tr	99.71	98.5	1.0	0.5
7	202	54.0	2.76	68.0	7.6	91.8	86.5	13.5	tr	99.79	98.2	1.2	0.6
8	251	54.0	2.76	71.6	5.8	89.4	84.7	15.3	tr	99.73	98.3	1.0	0.7
9	200	62.2	3.45	68.1	12.4	87.0	93.4	6.6		99.5	96.5	1.6	1.9
10	200	54.0	3.45	68.2	7.2	92.3	88.6	11.4		99.6	97.9	0.9	1.2
11	200	49.9	3.45	68.4	4.9	94.6	85.4	14.6		99.5	98.0	0.6	1.4
12	200	41.0	3.45	68.0	1.4	98.0	77.8	22.2		99.4	98.8	0.2	1.00
13	200	32.0	3.45	68.3	0.1	99.3	67.3	32.7		99.8	99.5	0.0	0.50
0.5 atm													
14	83	54.0	2.76	47.4	0.0	100	92.1	7.9	0	99.84	83.2	0.0	16.8
15	100	54.0	2.76	54.6	0.3	99.5	90.8	9.2	0	99.76	91.1	0.1	8.8
16	141	54.0	2.76	64.1	3.1	96.5	88.3	11.7	tr	99.81	97.4	0.5	2.1
17	161	54.0	2.76	67.1	5.5	93.6	87.4	12.6	tr	99.47	98.2	0.9	0.9
18	183	54.0	2.76	69.1	5.5		86.3	13.6	tr	99.76	98.7	0.8	0.4
19	196	54.0	2.76	70.2	5.6	91.0	86.1	13.9	tr	99.82	99.2	0.7	0.1
0.07 atm													
20	80	54.0	2.76	62.2	0.4	99.1	88.4	11.6	0	99.62	95.7	0.0	4.3
21	100	54.0	2.76	65.5	0.5	98.6	87.4	12.6	0	99.71	97.8	0.0	2.2
22	121	54.0	2.76	67.0	2.4	96.0	86.6	13.4	0	99.73	97.5	0.4	2.1
23	141	54.0	2.76	70.4	0.8	97.3	85.7	14.3	0	99.66	98.6	0.1	1.3
24	161	54.0	2.76	72.3	1.8	92.9	84.8	15.2	0	99.81	98.9	0.3	0.8
25	181	54.0	2.76	73.2	0.8	68.7	84.2	15.8	0	99.83	99.0	0.1	0.2
26	196	54.0	2.76	74.6	1.3	68.4	83.6	16.4	0	99.60	98.6	0.2	1.2
27	200	52.0	2.76	74.3	1.4	69.5	82.4	17.6		99.8	99.3	0.2	0.5
28	200	52.0	3.45	73.7	2.3	75.0	85.3	14.7		99.8	99.1	0.3	0.6
29	200	52.0	4.14	73.6	3.4	71.7	87.4	12.6		99.7	99.0	0.4	0.6
30	200	48.0	2.76	74.6	1.7	63.3	78.5	21.5		99.9	99.3	0.3	0.4
31	200	48.0	3.45	74.4	1.8	65.1	81.8	18.2		99.9	99.2	0.2	0.6
32	200	48.0	4.14	74.5	1.6	66.2	84.1	15.6		99.8	98.8	0.2	1.0

<sup>a</sup> Includes methanol not distilled from the acid.

accounted for as distillate and as monomethylphosphoric acid.

During the precipitation and filtration stages of the process, acid and methanol may be in contact for several hours at the reaction temperature. To determine if esterification occurs under these conditions, mixtures of methanol with acids of different concentrations were held at 72°C for 92 hr. The results showed that no esterification occurs during the precipitation and filtration phase of the process with 54% P<sub>2</sub>O<sub>5</sub> acid, but if the acid is highly concentrated some esterification occurs even at low temperature.

In other tests filtrate from the continuous purification of green wet-process acid was distilled to a temperature of 200°C at 1 atm and at 0.07 atm. The raw acid contained 54% P<sub>2</sub>O<sub>5</sub> and its purification was made with the mole ratio N:P of 0.178 and with the weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of 3.2. The acid residue from distillation at 1.00 atm contained 62.6% P<sub>2</sub>O<sub>5</sub> and 4.6% of the P was esterified; that from distillation at 0.07 atm contained 69.1% P<sub>2</sub>O<sub>5</sub> and only 1.5% of the P was esterified. Esterification of the purified acid was about the same as that obtained with reagent-grade acid distilled under the same conditions. The concentration of P<sub>2</sub>O<sub>5</sub> in the residues was lower than that in the corresponding reagent grade acid; this evidently resulted from the impurities, particularly ammonia, remaining with the acid and lowering the vapor pressure. The ratio F:P<sub>2</sub>O<sub>5</sub> in the acid residue was lower than in the undistilled filtrate, which indicates that some fluorine distills with the methanol.

Since it appeared that some esterification of the acid is unavoidable, technical grade monomethylphosphoric acid was evaluated in the greenhouse as a phosphorus source for corn. The results showed that the ester was at least equivalent to conventional phosphate sources. It thus appears that small amounts of the ester in purified acid would have no adverse agronomic effects.

These studies indicate that the only significant reaction between methanol and phosphoric acid during distillation is the formation of monomethylphosphoric acid and trace amounts of dimethyl ether. Purified 54% wet-process acid prepared by batch distillation at atmospheric pressure will be esterified to the extent of about 6%, which is equivalent to a chemical loss of methanol of about 54 lb/ton of P<sub>2</sub>O<sub>5</sub>. Distillation under high vacuum reduces esterification to less than 2%, which corresponds to the chemical loss of less than 18 lb of methanol/ton of P<sub>2</sub>O<sub>5</sub>. Only simple batch distillations were studied; in a commercial process, continuous distillation would be used. In the batch distillation, methanol and acid were in contact at temperatures where esterification occurs for as long as 13 min. Furthermore, when esterification temperatures were reached, the acid was considerably depleted in water. Continuous distillation processes can be designed to minimize both of these factors, which should appreciably decrease esterification.

#### DISCUSSION OF RESULTS

Results from the laboratory study demonstrated the feasibility of continuous operation of the process to yield

H<sub>3</sub>PO<sub>4</sub> suitable for production of solution fertilizers. For most acids, mole ratio N:P of about 0.175 and weight ratio CH<sub>3</sub>OH:P<sub>2</sub>O<sub>5</sub> of about 3.5 appear to be about optimum for maximum purification with good filtration. A retention time of about 50 min and a minimum temperature of about 50°C are required for good filtration. For most acids these conditions will yield purified acids containing about 1 g of Fe, 0.5 g of Al, and 1.4 g of F/kg of P<sub>2</sub>O<sub>5</sub>. The removal of Mg depends upon the ratio F:Mg in the raw acid. Up to 90% of the Mg is removed from acids with high ratios of F:Mg, but as little as 20% of Mg is removed from acids with low ratios of F:Mg.

The methanol precipitates contained 46 to 54% P<sub>2</sub>O<sub>5</sub> and 4 to 6% nitrogen. All the phosphate was available and about 50% was water soluble by official AOAC procedures. Results from greenhouse tests showed that the precipitates were only slightly less effective than conventional phosphorus sources for corn.

Results from distillation studies showed that the only significant reaction of methanol with phosphoric acid was the formation of monomethylphosphoric acid. Under some conditions dimethyl ether also was formed, but only trace amounts that consume negligible amounts of methanol were formed under normal distillation conditions. Esterification increased with rising temperature and increasing concentration. It was minimized by distillation under vacuum and was virtually eliminated at lower acid concentrations. Distillation of methanol from purified

53% P<sub>2</sub>O<sub>5</sub> acid at atmospheric pressure resulted in the esterification of 4.4% of the acid, but in distillation at 0.07 atm only 1.5% of the acid was esterified. These esterification values are equivalent to methanol losses of 40 and 14 lb/ton of P<sub>2</sub>O<sub>5</sub>, respectively.

Greenhouse tests of technical grade monomethylphosphoric acid as a phosphorus source for corn showed that the ester was equivalent to conventional sources. Thus, small amounts of the ester in the purified acid would be expected to have no adverse agronomic effect.

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Received for review June 30, 1975. Accepted August 28, 1975.

## Chemistry of Tobacco Constituents. Oxidation of $\alpha$ -Ionone and the Acid-Catalyzed Rearrangement of 5-Keto- $\alpha$ -ionone

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A biosynthetic type synthesis from 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one ( $\alpha$ -ionone) of some of the cyclic compounds which occur in tobacco and other species has been investigated. Oxidation of  $\alpha$ -ionone gave 5-keto- $\alpha$ -ionone, 4-keto- $\beta$ -ionone, and the tobacco constituent,  $\beta$ -ionone epoxide. In aqueous organic acids, 5-keto- $\alpha$ -ionone cyclizes to 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone, which on reduction and dehydration yielded another natural product of tobacco, 1,2-dihydro-1,1,6-trimethylnaphthalene. Aerial oxidation of 4,4,7-trimethyl-3,4-dihydro-2(1*H*)-naphthalenone gave 4,4,7-trimethyl-1,4-dihydro-2-hydroxy-1-naphthalenone which has not been described previously.

A number of isoprenoid compounds have been identified in tobacco and its smoke condensate (Stedman, 1968; Tso, 1974). Several of these compounds have been shown to influence the aroma and flavor of tobacco smoke (Demole and Berthet, 1971). Although the biosynthetic origin of cyclic compounds as exemplified by 1,3,7,7-tetramethyl-2-oxabicyclo[4.4.0]dec-5-en-9-one (Figure 1, I) and 1,2-dihydro-1,1,6-trimethylnaphthalene (Figure 1, II) in tobacco (Demole and Berthet, 1972; Kimland et al., 1972) and other plants (Kemp et al., 1971) is uncertain, they may be derived from carotenoids via the intermediate flavor related  $\alpha$ -ionone, 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (Figure 1, III) and  $\beta$ -ionone, 4-(2,6,6-tri-

methyl-1-cyclohexen-1-yl)-3-buten-2-one (Figure 1, IV) by sequential oxidation, rearrangement, and reduction reactions.

To test the mechanistic feasibility of this proposal, we have reexamined the oxidation of  $\alpha$ -ionone and investigated the products formed by protonation and subsequent reduction of the oxidation products in aqueous media. This reaction sequence yielded a cyclic product identical with the natural constituent II found in tobacco (Kimland et al., 1972).

#### METHODS

**Chemicals.**  $\alpha$ -Ionone was obtained from Dodge and Olcott, Inc., New York, N.Y. All solvents used were of reagent grade.

**Spectra.** The NMR spectra were run in CDCl<sub>3</sub> solutions with a Varian HA-100 spectrometer. Infrared spectra were run on a Perkin-Elmer Model 237 spectrometer. High-resolution mass spectra were obtained on a CEC Model 110 spectrometer at 70 eV.

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