Literature Cited

(1) Laba, V. I.; Kron, A. A.; Prilezhayeva, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, No. 7, 1546.
(2) Killian, D. B.; Hennion, G. F., Nieuwland, J. A. *J. Am. Chem. Soc.* **1934**, *56*, 1384.
(3) Nazarov, I. N.; Makin, S. M.; Krouptsov, B. K.; Mironov, V. A. *Zh. Obshch. Khim.* **1959**, *29*, 106.
(4) Rozhkov, I. N.; Makin, S. M. *Zh. Obshch. Khim.* **1964**, *34*, 59.
(5) Bunina-Krivorukova, L. I.; Petrov, A. A. *Zh. Obshch. Khim.* **1963**, *33*, 427.
(6) Nazarov, I. N.; Gusev, B. P.; Gunar, V. I. *Zh. Obshch. Khim.* **1958**, *28*, 1444.
(7) Sancy, G.; Marbet, R. *Helv. Chim. Acta* **1967**, *50*, 1158.
(8) Shnaidman, L. O. *Proizvodstvo Vitaminov*; Khimia: Moscow, 1973; p 437.
(9) Serpinsky, V. V.; Voitkevich, S. A.; Luboshic, N. Yu. *Zh. Fiz. Khim.* **1957**, *31*, 1278.
(10) Dreisbach, R. R.; Martin, K. A. *Ind. Eng. Chem.* **1949**, *41*, 2875.
(11) Waradzin, W.; Skubla, P. *Chem. Prum.* **1973**, *23*, 556.
(12) Safo, K.; Kurihara, J.; Abe, S. *J. Org. Chem.* **1963**, *28*, 45.
(13) Gadzhiyev, S. N.; Kerimov, K. K.; Goubareva, A. I.; Beregovykh, V. V.; Ignatiyev, V. L.; Nurullayev, G. G. *Khim.-Farm. Zh.* **1982**, *16*, 1131.
(14) Maurit, M. E.; Smirnova, G. V.; Parfeonov, E. A.; Sarycheva, I. K.; Preobrazhensky, N. A. *Dokl. Akad. Nauk SSSR* **1961**, *140*, 1330.
(15) Weichet, J.; Hodrova, J.; Kvita, V. *Chem. Listy* **1957**, *51*, 568.
(16) Demole, E. *Compt. Rend.* **1956**, *243*, 1883.
(17) Arnold, L.; Pasedach, H.; Pommer, H. German Patent 1 793 037, 1968.
(18) Baudoin, M.; Perron, R. French Patent 2 327 980, 1975.
(19) Souvorov, L. V. *Termodynamika Gasovogo Sostoyaniya*; Khimia: Leningrad, 1970; p 230.
(20) Baglay, A. K.; Gurarly, L. L.; Kuleshov, G. G. *Khim.-Farm. Zh.* **1984**, *18*, 1013.
(21) Adamson, A. *Physical Chemistry of Surfaces*; Mir: Moscow, 1979; p 568.
(22) Beregovykh, V. V.; Gurarly, L. L.; Belousov, V. P. *Khim.-Farm. Zh.* **1986**, *20*, 1146.
(23) *Spravochnik Khimika*; Nikolskiy, B. P., Ed.; Khimia: Moscow, 1966; Vol. I, p 1071.
(24) Vasiliev, I. A.; Petrov, V. M. *Termodynamicheskiye Svoistva Kislorodsoderzhashchikh Organicheskikh Soyedinenly*, Khimia: Leningrad, 1984; p 320.
(25) Filippov, L. P. *Issledovaniye Teploprovodnosti Zhidkostey*; Moscow State University: Moscow, 1970; p 286.
(26) Rastorguyev, Yu. L.; Geller, V. Z. *Inzh.-Fiz. Zh.* **1967**, *13*, 17.
(27) Beregovykh, V. V., Geller, V. Z.; Kuleshov, G. G. *Khim.-Farm. Zh.* **1985**, *19*, 1517.
(28) Vargaftik, N. B. *Teplofizicheskiye Svoistva Zhidkostey i Gasov*; Nauka: Moscow, 1972; p 720.
(29) *Kratkiy Khimicheskiy Spravochnik*; Rabinovich, V. A., Ed.; Khimia: Leningrad, 1978; p 392.
(30) *Kratkiy Spravochnik Fiziko-Khimicheskikh Velichin*; Mishchenko K. P., Ravdel, A. A., Eds.; Khimia: Leningrad, 1967; p 184.
(31) Mustafayev, R. A. *Teplofisicheskiye Svoistva Uglevodorodov pri Vysokikh Parametrakh Sostoyaniya*; Energiya: Moscow, 1969; p 324.
(32) Filippov, L. P. In *Obzory po Teplofizicheskim Svoistvam Veshchestv*; AN SSSR: Moscow, 1977; No. 2, pp 1-108.
(33) Collerson, R. R. *J. Chem. Soc.* **1965**, 3697.
(34) Ambrose, D. *J. Appl. Chem. Biotechnol.* **1974**, *24*, p 359.
(35) Hales, J. L. *Trans. Faraday Soc.* **1967**, *63*, 1876.
(36) Markovnik, V. A. *Termodinamika Organicheskikh Soyedineniy*; N. I. Lobachevski State University Gorkij, 1979; No. 8, p 107.
(37) Nazarov, I. N. *Zh. Obshch. Khim.* **1959**, *29*, p 3683.
(38) Timmermans, J. *J. Chem. Phys.* **1932**, *29*, (10), 529.
(39) Fernandez, J. E. *Chem. Rev.* **1962**, *62*, 485.
(40) Martynenko, V. I. *Funkzionalnyje Organicheskiye Soyedineniya i Polimery*; Polytechnical Institute: Volgograd, 1975; p 296.

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Phase Systems Melamine–H_3PO_4–H_2O and Melamine–NH_3–H_3PO_4–H_2O at 25 °C

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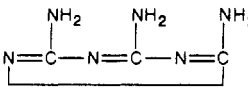
The $C_3H_6N_6$–H_3PO_4–H_2O and $C_3H_6N_6$–NH_3–H_3PO_4–H_2O phase systems were determined from 0 to 50% P_2O_5 at 25 °C. Eleven adducts between melamine and H_3PO_4/$NH_4H_2PO_4$ were isolated, identified, and characterized crystallographically. Below 10% P_2O_5, the solubility of melamine in these systems was less than 0.3%. Above 30% P_2O_5, the solubility of melamine ranged up to about 8%. The results indicate that the precipitation of melamine–phosphoric acid adducts, especially $C_3H_6N_6 \cdot H_3PO_4$, provides a practical process for purifying wet-process phosphoric acid.

Melamine ($C_3H_6N_6$, eq 1) readily forms insoluble adducts with many organic and inorganic acids (*1*, *2*) and has been proposed as a purification and collection agent in many acid reclamation processes (*3*-*7*). Melamine also has been proposed



(1)

as an agent for producing linear and cyclic polyphosphate compounds (*8*). Since the stability of impure wet-process phosphoric acid (WPA) and liquid fertilizers prepared from this acid is limited by dissolved impurities, particularly magnesium [which has a very low saturation composition in fluid fertilizers (*9*)], it seemed feasible that a purification scheme could be developed using melamine.

Thus, a recently developed process (*3*, *4*) has been proposed for this purpose. The process consists of precipitating acidic melamine phosphates from phosphoric acid solutions and subsequently recovering the melamine in aqueous ammonium hydroxide/phosphate solutions. This reclamation process traverses the phase system $C_3H_6N_6$–NH_3–H_3PO_4–H_2O from highly acidic to weakly basic conditions. Phase chemistry data are not available to describe the chemical properties and compositions of the reaction products that will be encountered by the interaction of these materials. A few of the adducts have been encountered, but the characterization data to distinguish them are not available (*10*-*12*).

Experimental Section

To understand the melamine precipitation and regeneration process for the purification of WPA (*3*, *13*), a major research study was conducted to characterize the chemical and physical properties of the equilibrating solids in the systems $C_3H_6N_6$–H_3PO_4–H_2O and $C_3H_6N_6$–NH_3–H_3PO_4–H_2O at 25 °C.

Early in the study it became apparent that numerous unknown materials would be encountered (*1*-*3*). Thus, the initial task was to synthesize and characterize homogeneous samples of each melamine–phosphoric acid adduct. For this phase of the study, a strong reagent-grade H_3PO_4 solution (60% P_2O_5)

Table I. Chemical Analysis of Solid Phases

sample no.	wt %				mol/mol of PO_4		
	Mel–N	NH_3–N	P_2O_5	H_2O^a	melamine	H_2O	NH_3
1	42.3		17.4	12.53	2.06	2.84	
$Mel_2{\cdot}H_3PO_4{\cdot}3H_2O$	41.58		17.57	13.57	2.00	3.00	
1	40.7	0.6	20.6	10.52	1.643	2.01	nil
2	40.2		20.4	11.54	1.666	2.231	
$Mel_5{\cdot}(H_3PO_4)_3{\cdot}6H_2O$	40.70	0	20.64	10.47	1.667	2.00	
1	38.8		21.9	11.56	1.497	2.028	
2	38.9		22.0	11.28	1.494	2.022	
$Mel_3{\cdot}(H_3PO_4)_2{\cdot}4H_2O$	39.01		21.98	11.15	1.500	2.00	
1	39.4		25.0	6.39	1.332	1.008	
2	39.1		24.9	6.98	1.327	1.106	
$Mel_4{\cdot}(H_3PO_4)_3{\cdot}3H_2O$	39.44		25.00	6.34	1.333	1.00	
1	38.2		27.0	5.43	1.196	0.793	
2	38.1		26.7	6.00	1.206	0.887	
$Mel_6{\cdot}(H_3PO_4)_5{\cdot}4H_2O$	38.24		26.93	5.46	1.20	0.80	
1	37.3		31.6	0.43	0.998	0.008	
2	37.3		31.7	0.10	1.000	0.002	
$Mel{\cdot}H_3PO_4$	37.50		31.70	0.00	1.000	0.00	
1	27.2		42.3	0.81	0.505	0.07	
2	24.2		44.5	2.28	0.460	0.202	
$Mel{\cdot}(H_3PO_4)_2$, A	26.09		44.10	0.00	0.500	0.00	
1	24.5		43.5	3.21	0.477	0.290	
2	24.8		43.4	2.76	0.482	0.250	
$Mel{\cdot}(H_3PO_4)_2$, B	26.09		44.10	0.00	0.500	0.00	
1	19.5		30.9	28.1	0.533	3.59	
$Mel{\cdot}(H_3PO_4)_2{\cdot}6H_2O$	19.53		33.02	25.12	0.500	3.00	
1	16.2		52.65	16.38	0.26	0.91	
$Mel{\cdot}(H_3PO_4)_4$	16.22		54.83	0.00	0.25	0.00	
1	30.6	4.8	25.5	11.63	1.014	1.77	0.954
2	30.5	4.8	25.3	13.47	1.019	2.10	0.961
$Mel{\cdot}NH_4H_2PO_4{\cdot}2H_2O$	30.77	5.13	26.01	13.19	1.00	2.00	1.00

[a] Hydrated H_2O.

Table II. Optical Data

compound	crystal system, class, and habit	refractive indices	optical properties
$Mel_2{\cdot}H_3PO_4{\cdot}3H_2O$	triclinic, 1; (010) plate crystals elongated along a and modified by {011} and {101}; twins on (001) with perfect cleavage parallel to (100)	$\alpha = 1.456$; $\beta = 1.707$; $\gamma = 1.738$	biaxial (–), $2V = 34°$; OAP almost $\perp$ (010) with $X' \sim X \wedge a = 18°$ in obtuse β, $\angle\beta = 109°$; $Z' \sim Z \wedge b = 3°$ in acute γ; $d = 1.62$
$Mel_5{\cdot}(H_3PO_4)_3{\cdot}6H_2O$	orthorhombic, mmm; plate crystals tabular on X–Z plane and exhibiting (100), (010), and (001) perfect cleavage along both directions of tabular plane	$\alpha = 1.458$; $\beta = 1.696$; $\gamma = 1.730$	biaxial (–), $2V = 37°$; OAP = tabular plane; $d_{calcd} = 1.63$
$Mel_3{\cdot}(H_3PO_4)_2{\cdot}4H_2O$	monoclinic, $2/m$; prismatic crystals, tabular on 010 and exhibiting (100), (010), and {011}	$\alpha = 1.460$; $\beta = 1.683$; $\gamma = 1.716$	biaxial (–), $2V = 38°$; OAP $\perp$ (010), $X \wedge c = 9°$ in acute β, $\beta = 117°$; $d = 1.63$
$Mel_4{\cdot}(H_3PO_4)_3{\cdot}3H_2O$	orthorhombic, mmm; sealer crystals, tabular on X–Z plane	$\alpha = 1.465$; $\beta = 1.707$; $\gamma = 1.727$	biaxial (–), $2V = 28°$; OAP = tabular plane; $d_{calcd} = 1.68$
$Mel_6{\cdot}(H_3PO_4)_5{\cdot}4H_2O$	monoclinic, $2/m$; plate crystals tabular on (010), elongated along c and modified by {111}, {110}, {101}, and (100)	$\alpha = 1.460$; $\beta = 1.697$; $\gamma = 1.723$	biaxial (–), $2V = 33°$; OAP = (010), $Y = b$; $X \wedge c = 28°$ in obtuse β, $\beta = 91°$; weak disp., $r < V$, $d = 1.69$
$Mel{\cdot}H_3PO_4$	triclinic, 1, (110) plate crystals elongated along c, modified by (010) and (100); twins on (110)	$\alpha = 1.442$; $\beta = 1.690$; $\gamma = 1.741$	biaxial (–), $2V = 43°$; OAP = (010), $Y' \sim Y = b$, $\beta = 126°$; $d = 1.72$; $Z \wedge c = 46°$ in acute β
$Mel{\cdot}(H_3PO_4)_2$, A	monoclinic, $2/m$; (010) tablets slightly elongated along c and terminated by (100) and (001)	$\alpha = 1.436$; $\beta = 1.596$; $\gamma = 1.691$	biaxial (–), $2V = 69°$; $\beta = 119°$, OAP = (010); $d = 1.79$
$Mel{\cdot}(H_3PO_4)_2$, B	orthorhombic, mmm; rectangular plates elongated along X and modified by (100), (001), and (010)	$\alpha = 1.551$; $\beta = 1.591$; $\gamma = 1.616$	biaxial (–), $2V = 75°$; OAP and $X \perp$ tabular plane; $d_{calcd} = 1.84$
$Mel{\cdot}(H_3PO_4)_2{\cdot}6H_2O$	orthorhombic, mmm; plate crystals tabular on Y–Z plane	$\alpha = 1.470$; $\beta = 1.588$; $\gamma = 1.637$	biaxial (–), $2V = 61°$; OAP and $X \perp$ tabular plane; $d_{calcd} = 1.72$
$Mel{\cdot}(H_3PO_4)_4$	monoclinic, $2/m$; highly modified prisms	$\alpha = 1.448$; $\beta = 1.595$; $\gamma = 1.609$	biaxial (–); OAP = (010); $d_{calcd} = 1.91$
$Mel{\cdot}NH_4H_2PO_4{\cdot}2H_2O$	triclinic, 1; (010) plate crystals elongated along c and modified by (100), (001), (101), and (101)	$\alpha = 1.469$; $\beta = 1.652$; $\gamma = 1.670$	biaxial (–), $2V = 32°$; OAP $\sim$ (010), $X \wedge c = 17°$ in acute β, $\beta = 107°$; $d_{calcd} = 1.94$

Table III. Unit-Cell Data for Melamine Phosphates

contents of unit cell	crystal system	space group	lattice constants						calcd density, g/cm^3
			a_0	b_0	c_0	α	β	γ	
$2[C_3H_6N_6{\cdot}H_3PO_4]$	triclinic	$P1$ or $P\bar{1}$	9.343	10.220	4.578	89.9	93.8	83.7	1.717
$4[C_3H_6N_6{\cdot}(H_3PO_4)_2{-}A]$	monoclinic	$P\,2/a$	16.722	8.033	4.572	90.0	100.5	90.0	1.771
$2[(C_3H_6N_6)_2{\cdot}H_3PO_4{\cdot}3H_2O]$	triclinic	$P1$ or $P\bar{1}$	10.671	12.539	6.781	105.7	108.7	78.9	1.634
$4[(C_3H_6N_6)_6{\cdot}(H_3PO_4)_5{\cdot}4H_2O]$	monoclinic	$B2$, Bm, or $B\,2/m$	21.777	20.957	11.279	90.0	90.1	90.0	1.701
$2[C_3H_6N_6{\cdot}NH_4H_2PO_4{\cdot}2H_2O]$	triclinic	$P1$ or $P\bar{1}$	6.815	14.080	6.339	100.7	107.3	91.2	1.617

Table IV. X-ray Powder Diffraction Data of Melamine Phosphates[a]

d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0	d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0	d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0	d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0
							$Mel_2{\cdot}H_3PO_4{\cdot}3H_2O$								
11.95	11.989	010	3	4.448	4.449	2$\bar{1}$0	1	3.134	3.135	22$\bar{2}$	6	2.323	2.321	$\bar{3}$31	2
10.02	10.037	100	2	4.097	4.089	220	1		3.078	320		2.244	2.246	15$\bar{2}$	3
8.17	8.178	110	1	3.994	3.996	030	2	3.073	3.071	02$\bar{2}$	17	2.173	2.171	23$\bar{3}$	1
7.28	7.291	1$\bar{1}$0	22	3.958	3.956	$\bar{2}$11	3		3.071	14$\bar{1}$		2.156	2.156	4$\bar{1}$2	2
6.26	6.271	11$\bar{1}$	14	3.915	3.915	13$\bar{1}$	10	2.968	2.968	140	4		2.156	20$\bar{3}$	
	6.257	001		3.870	3.871	130	2	2.956	2.963	23$\bar{0}$	3	2.087	2.088	051	2
6.14	6.142	01$\bar{1}$	16	3.782	3.779	$\bar{1}$21	3		2.951	$\bar{1}$12		2.046	2.045	24$\bar{3}$	1
5.98	5.995	020	6	3.644	3.645	2$\bar{2}$0	7	2.896	2.895	131	14	2.025	2.025	$\bar{2}$13	4
5.43	5.432	120	34	3.523	3.525	121	6	2.789	2.791	$\bar{2}$12	15	1.989	1.988	$\bar{3}$32	1
5.10	5.104	12$\bar{1}$	1	3.384	3.391	11$\bar{2}$	7		2.787	3$\bar{2}$0		1.936	1.935	260	1
5.02	5.019	200	18		3.377	30$\bar{1}$		2.682	2.682	321	5	1.785	1.785	05$\bar{3}$	3
4.92	4.922	$\bar{1}$11	16	3.327	3.324	310	15	2.553	2.552	24$\bar{2}$	2	1.713	1.716	5$\bar{3}$0	3
4.83	4.834	210	2	3.263	3.263	10$\bar{2}$	16	2.515	2.515	410	3		1.710	50$\bar{3}$	3
4.75	4.756	21$\bar{1}$	4		3.263	12$\bar{2}$		2.418	2.417	420	13	1.702	1.702	213	2
4.74	4.738	101	3	3.215	3.216	21$\bar{2}$	100	2.392	2.396	150	2	1.607	1.607	$\bar{5}$32	3
4.618	4.608	20$\bar{1}$	7												
							$Mel_6(H_3PO_4)_5{\cdot}4H_2O$								
10.01	10.007	101	2	4.385	4.388	032	1		3.215	$\bar{2}$52		2.379	2.379	713	2
9.64	9.662	210	2	4.297	4.294	430	13	3.182	3.183	$\bar{3}$23	13		2.378	472	
9.03	9.043	$\bar{1}$11	5	4.065	4.066	$\bar{5}$01	5	3.146	3.139	$\bar{4}$42	5	2.359	2.359	$\bar{4}$34	1
	9.030	111		3.996	3.991	$\bar{5}$11	11	3.027	3.026	$\bar{1}$43	5	2.269	2.269	$\bar{7}$33	1
7.24	7.243	$\bar{1}$21	2	3.912	3.913	402	2	2.986	2.984	640	7	2.212	2.212	614	3
	7.237	121			3.912	$\bar{2}$50		2.865	2.864	262	5	2.180	2.180	$\bar{6}$24	1
5.86	5.866	$\bar{3}$11	6	3.848	3.846	412	12	2.801	2.799	$\bar{6}$32	3	2.152	2.152	$\bar{2}$64	5
	5.855	311		3.785	3.786	521	4	2.748	2.749	$\bar{5}$23	1		2.151	$\bar{4}$54	
5.72	5.728	131	<1	3.711	3.706	$\bar{1}$03	14	2.642	2.644	072	5		2.062	145	
5.64	5.640	002	<1	3.655	3.650	$\bar{1}$13	12		2.640	224		2.062	2.062	$\bar{3}$83	2
5.44	5.444	400	10	3.516	3.514	$\bar{5}$31	25	2.619	2.620	080	6		2.062	573	
5.24	5.239	040	100	3.491	3.492	123	51		2.615	034		1.961	1.961	$\bar{8}$04	3
5.02	5.034	330	2	3.415	3.414	432	5	2.544	2.544	$\bar{2}$34	3	1.854	1.853	$\bar{2}$06	1
	5.012	$\bar{2}$02		3.336	3.336	303	44	2.536	2.536	830	1		1.668	606	
4.96	4.966	022	1	3.296	3.298	161	43		2.534	181		1.666	1.666	$\bar{5}$75	5
4.65	4.643	$\bar{1}$41	4		3.294	313		2.512	2.517	660	2		1.665	$\bar{6}$16	
4.527	4.521	$\bar{2}$22	3	3.218	3.221	630	5	2.422	2.422	$\bar{2}$44	4				
							$Mel{\cdot}H_3PO_4$								
10.14	10.157	010	15	3.392	3.386	030	31	2.511	2.513	1$\bar{3}$1	2	2.020	2.019	430	2
9.25	9.265	100	12	3.361	3.368	20$\bar{1}$	33	2.469	2.465	311	3	2.006	2.012	401	5
7.25	7.257	110	69	3.305	3.309	12$\bar{1}$	8	2.443	2.435	32$\bar{1}$	6		1.999	$\bar{3}$31	
6.49	6.496	1$\bar{1}$0	3	3.173	3.180	$\bar{1}$21	10	2.421	2.419	330	3	1.944	1.941	250	4
5.08	5.079	020	15	3.130	3.129	$\bar{2}$11	6	2.359	2.360	3$\bar{1}$1	8	1.913	1.917	3$\bar{3}$1	3
4.673	4.677	120	57	3.084	3.088	300	26	2.342	2.339	240	1	1.854	1.853	151	4
4.634	4.632	200	53		3.079	1$\bar{3}$0		2.235	2.233	012	7		1.853	500	
4.401	4.403	210	21	2.940	2.939	310	25	2.208	2.208	11$\bar{2}$	3	1.812	1.811	431	3
4.262	4.259	1$\bar{2}$0	58	2.870	2.869	3$\bar{1}$0	16	2.136	2.136	$\bar{1}$41	11	1.792	1.791	350	1
4.197	4.211	$\bar{1}$01	3	2.746	2.733	031	8	2.119	2.119	1$\bar{1}$2	3	1.777	1.775	251	1
	4.181	011		2.697	2.694	13$\bar{1}$	6	2.073	2.073	12$\bar{2}$	2	1.710	1.713	44$\bar{1}$	4
4.140	4.150	01$\bar{1}$	5	2.646	2.643	30$\bar{1}$	10	2.046	2.047	$\bar{1}$22	2		1.707	530	
4.005	3.991	101	11	2.617	2.615	31$\bar{1}$	2		2.045	$\bar{2}$12		1.658	1.660	441	4
3.969	3.948	11$\bar{1}$	6	2.561	2.582	2$\bar{2}$1	3	2.036	2.032	122	2		1.658	4$\bar{3}$1	
3.663	3.645	1$\bar{1}$1	100	2.543	2.539	040	7	2.029	2.031	42$\bar{1}$	2	1.561	1.559	26$\bar{1}$	3
3.633	3.629	220	58												
							$Mel{\cdot}(H_3PO_4)_2$, Form A								
8.18	8.221	200	19	3.050	3.043	510	9	2.348	2.343	511	3	1.915	1.915	630	2
8.02	8.033	010	95	3.001	3.012	12$\bar{1}$	14	2.276	2.276	20$\bar{2}$	5	1.892	1.891	42$\bar{2}$	2
4.56	4.553	10$\bar{1}$	18		2.995	021		2.259	2.264	620	7	1.851	1.849	63$\bar{1}$	1
4.527	4.527	310	85	2.935	2.931	22$\bar{1}$	12	2.251	2.250	131	6	1.841	1.843	222	1
4.022	4.017	020	90	2.920	2.920	50$\bar{1}$	10	2.145	2.146	31$\bar{2}$	1	1.816	1.817	52$\bar{2}$	4
3.927	3.923	011	21	2.777	2.774	32$\bar{1}$	9		2.144	40$\bar{2}$		1.769	1.762	241	3
3.837	3.836	30$\bar{1}$	100	2.746	2.744	51$\bar{1}$	7	2.080	2.076	202	1	1.725	1.723	44$\bar{1}$	3
3.690	3.685	111	3	2.718	2.710	221	10	2.032	2.037	50$\bar{2}$	1	1.677	1.678	512	1
3.660	3.659	410	2	2.649	2.643	130	8	2.014	2.008	212	2	1.656	1.655	54$\bar{1}$	2
3.617	3.609	220	24	2.552	2.556	60$\bar{1}$	3	1.989	1.993	140	4	1.644	1.640	232	3
3.460	3.462	31$\bar{1}$	3	2.508	2.503	321	2	1.984	1.985	12$\bar{2}$	4	1.581	1.580	332	3
3.349	3.354	40$\bar{1}$	15	2.437	2.436	61$\bar{1}$	11	1.955	1.958	302	3	1.474	1.474	641	2
	3.340	211		2.410	2.406	330	2		1.951	240		1.410	1.408	55$\bar{1}$	1
3.098	3.095	41$\bar{1}$	5	2.365	2.362	52$\bar{1}$	5	1.919	1.918	60$\bar{2}$	3	1.406	1.407	213	2
							$Mel{\cdot}NH_4H_2PO_4{\cdot}2H_2O$								
6.92	6.899	020	85	4.931	4.926	$\bar{1}$20	17	3.972	3.968	1$\bar{2}$1	12	3.234	3.234	21$\bar{1}$	22
6.08	6.060	$\bar{1}$10	15	4.728	4.733	$\bar{1}$11	20	3.902	3.902	130	15	3.193	3.191	$\bar{2}$11	18
5.94	5.929	001	64	4.600	4.597	030	61	3.651	3.669	13$\bar{1}$	21	3.140	3.151	$\bar{1}$40	53
5.71	5.695	110	19	4.410	4.424	12$\bar{1}$	5	3.632	3.632	1$\bar{2}$1	25	3.107	3.117	11$\bar{2}$	5
5.08	5.089	011	15	4.120	4.107	021	4	3.453	3.448	040	68		3.101	210	
5.01	5.021	02$\bar{1}$	9	4.028	4.047	03$\bar{1}$	5	3.303	3.303	20$\bar{1}$	100	3.032	3.032	$\bar{2}$20	11

Table IV (Continued)

d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0	d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0	d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0	d_{obsd}, Å	d_{calcd}, Å	hkl	I/I_0
2.997	3.006	$12\bar{2}$	14	2.392	2.399	$23\bar{2}$	4	1.986	1.984	$\bar{2}42$	3	1.699	1.700	$33\bar{3}$	4
2.940	2.945	$\bar{2}21$	6	2.380	2.377	$\bar{1}32$	2	1.973	1.976	003	2	1.669	1.669	$15\bar{2}$	2
2.823	2.823	$14\bar{1}$	5	2.342	2.344	$13\bar{2}$	25	1.930	1.936	$2\bar{2}2$	2	1.650	1.649	$\bar{1}43$	7
2.762	2.758	050	18	2.302	2.305	$06\bar{1}$	3		1.927	$23\bar{3}$		1.618	1.619	123	3
2.726	2.721	$23\bar{1}$	16	2.206	2.206	$24\bar{1}$	7	1.916	1.915	202	1		1.617	$42\bar{2}$	
2.650	2.647	$\bar{1}22$	6	2.128	2.123	$\bar{1}42$	6	1.905	1.904	013	2	1.614	1.614	$\bar{2}43$	2
2.618	2.615	$\bar{1}50$	14	2.120	2.114	160	5	1.862	1.861	$\bar{2}61$	3	1.574	1.576	$11\bar{4}$	2
2.558	2.563	$2\bar{1}1$	3	2.107	2.110	310	4	1.834	1.835	$26\bar{2}$	6	1.522	1.523	$2\bar{2}3$	2
	2.555	230		2.072	2.072	$31\bar{2}$	5		1.833	161		1.500	1.501	312	2
2.502	2.504	$2\bar{2}1$	8	2.025	2.027	$33\bar{1}$	5	1.816	1.816	$24\bar{2}$	2	1.498	1.499	$40\bar{3}$	3
2.446	2.445	$1\bar{2}2$	12		2.024	$\bar{1}61$		1.783	1.785	$05\bar{3}$	3	1.480	1.482	004	2
2.423	2.421	$24\bar{1}$	7												

[a] Copper Kα radiation, λ = 1.54178 Å; silicon powder (NBS No. 640), a_0 = 5.43088 Å, used as internal calibration standard. d_{obsd} is the observed d spacing; d_{calcd} is calculated from single-crystal data.

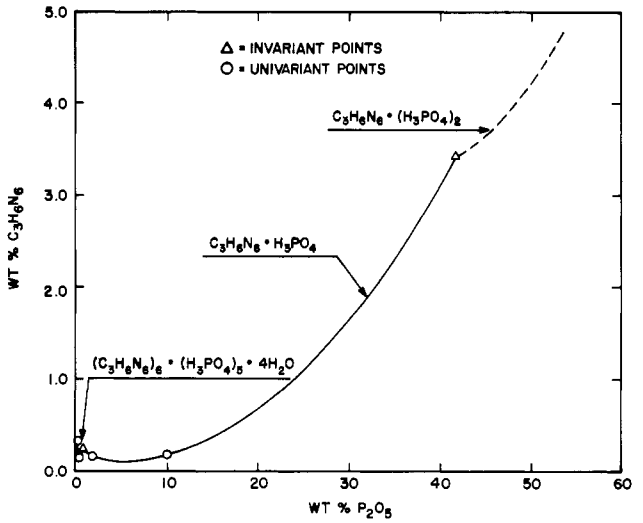


Figure 1. System $C_3H_6N_6$–H_3PO_4–H_2O at 25 °C.

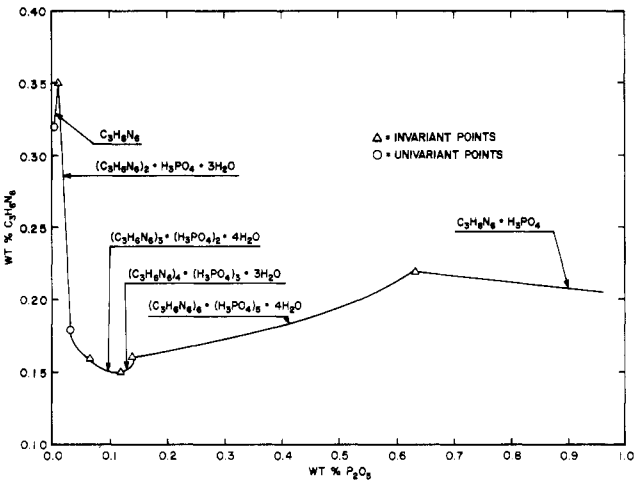


Figure 2. System $C_3H_6N_6$–H_3PO_4–H_2O at 25 °C.

was concentrated to about 70% P_2O_5 and then saturated with a high-grade melamine product. The melamine reagent was homogeneous and well crystallized and possessed the optical and X-ray properties for pure melamine (*14*). The saturating melamine–phosphoric acid adduct in this concentrated acid solution was very soluble, and the crystals could be developed into coarse, euhedral units by standard crystal-growing techniques.

After separation, the unique crystalline phase was characterized chemically and crystallographically (optical microscopy and X-ray diffraction) for future identification. As increasing quantities of melamine were charged to the slurry, the total H_3PO_4 in solution decreased and the stable solid phases changed either to other crystalline materials having a higher ratio melamine:H_3PO_4 or to another dimorphic form. In turn, each new phase was grown as coarse crystals and isolated for characterization.

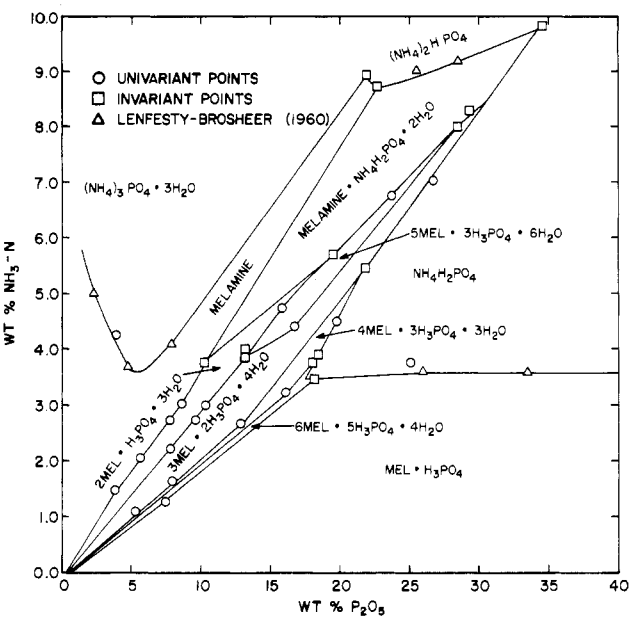


Figure 3. Phase system $C_3H_6N_6$–NH_3–H_3PO_4–H_2O at 25 °C.

During this phase of the study, a slurry sample representing the invariant points (two phases) and an occasional univariant point representing a tie-line composition were set aside for equilibration. These samples were eventually analyzed and used to obtain the saturation isotherms at 25 °C for the $C_3H_6N_6$–H_3PO_4–H_2O phase system.

Another sample of concentrated H_3PO_4 was saturated with $NH_4H_2PO_4$ and melamine until the acidic adduct $C_3H_6N_6$·H_3PO_4 was a stable solid phase. This slurry then was ammoniated (while being monitored by optical microscopy methods) to obtain slurry samples containing two or three solid phases representing the tie-line and invariant point composition for the system $C_3H_6N_6$–NH_3–H_3PO_4–H_2O at 25 °C. Two new crystalline components were encountered in this study that were not present in the ammonia-free system. As before, these components were isolated for characterization.

The results of the solid-phase analysis are given in Table I. The more acidic adducts having a ratio H_3PO_4:melamine equal to or greater than 2 were stable in very viscous solutions above 50% P_2O_5 at 6–8% melamine. These solutions were difficult to equilibrate and this region of the phase system was not

Table V. X-ray Powder Diffraction Data of Melamine Phosphates[a]

d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0	d, Å	I/I_0
			$(Mel)_5(H_3PO_4)_3 \cdot 6H_2O$				
10.50	16	4.301	1	3.004	3	2.367	2
8.10	6	4.008	6	2.957	4	2.324	3
7.17	1	3.782	9	2.870	5	2.213	5
6.43	25	3.587	14	2.851	8	1.998	2
6.13	4	3.513	27	2.765	7	1.850	3
5.27	86	3.376	5	2.650	4	1.625	2
4.92	14	3.214	100	2.631	5	1.617	1
4.450	8	3.171	12	2.502	4	1.605	2
4.428	8						
			$(Mel)_3(H_3PO_4)_2 \cdot 4H_2O$				
10.77	3	4.266	10	2.954	5	2.182	1
10.18	4	3.960	19	2.920	1	2.154	3
8.93	16	3.813	3	2.906	1	2.136	2
6.12	1	3.760	3	2.718	7	2.025	1
5.84	4	3.682	7	2.683	1	1.983	4
5.57	6	3.615	9	2.660	3	1.975	2
5.42	35	3.565	2	2.600	6	1.902	2
5.30	8	3.501	11	2.536	4	1.877	2
5.18	3	3.408	2	2.505	1	1.873	1
5.09	1	3.248	100	2.445	2	1.803	3
4.99	1	3.162	5	2.382	1	1.690	2
4.882	12	3.125	2	2.259	1	1.624	3
4.676	3	3.066	1	2.245	2	1.544	1
4.486	2	2.992	9				
			$(Mel)_4(H_3PO_4)_3 \cdot 3H_2O$				
10.25	5	4.582	1	3.260	25	2.338	1
8.86	3	4.467	9	3.220	11	2.296	2
8.40	4	4.311	9	3.166	55	2.280	1
8.01	2	4.160	3	3.132	2	2.170	3
7.26	6	4.096	4	3.059	8	2.118	1
6.51	3	3.910	2	2.870	5	2.084	4
6.32	4	3.864	10	2.785	1	2.049	3
6.09	6	3.818	9	2.671	4	1.993	1
5.62	8	3.680	2	2.578	6	1.874	1
5.36	3	3.574	6	2.565	6	1.778	1
5.13	100	3.492	1	2.531	2	1.729	1
4.91	7	3.424	48	2.484	1	1.630	2
4.87	6	3.351	12				
			$Mel(H_3PO_4)_2$, Form B				
10.06	4	3.956	100	2.776	3	1.970	3
8.00	75	3.840	41	2.743	3	1.923	3
7.92	92	3.746	12	2.720	10	1.862	4
7.48	2	3.663	5	2.646	7	1.841	1
7.23	1	3.615	10	2.603	6	1.814	5
7.10	1	3.565	43	2.573	2	1.774	3
6.60	2	3.506	26	2.517	5	1.753	2
6.20	1	3.349	9	2.439	4	1.723	3
5.52	2	3.310	4	2.415	4	1.697	1
5.31	19	3.207	13	2.369	3	1.685	2
4.91	2	3.075	19	2.347	2	1.603	3
4.530	37	3.049	8	2.265	9	1.588	2
4.491	50	3.017	8	2.248	4	1.553	2
4.412	3	3.002	9	2.205	5	1.492	2
4.265	2	2.994	11	2.113	1	1.473	2
4.090	2	2.846	3	2.042	2	1.407	3
4.018	56	2.812	6	2.010	9	1.330	3
			$Mel(H_3PO_4)_2 \cdot 6H_2O$				
10.07	29	4.478	5	3.309	31	2.374	3
9.21	3	4.250	10	3.249	9	2.350	6
8.06	16	4.206	9	3.207	3	2.296	2
7.61	3	4.097	24	3.120	2	2.262	1
7.55	7	4.035	22	3.076	46	2.246	3
7.26	6	3.946	8	3.034	3	2.138	3
6.78	3	3.868	85	2.933	4	2.127	5
6.62	6	3.768	9	2.880	18	2.044	3
6.20	9	3.746	25	2.770	7	2.008	9
6.07	8	3.664	27	2.743	14	1.719	2
5.54	12	3.626	15	2.701	19	1.712	2
5.32	23	3.571	100	2.655	5	1.602	1
5.21	4	3.513	2	2.616	3	1.595	2
5.047	7	3.457	9	2.599	1	1.557	3
4.720	8	3.391	12	2.564	6	1.373	2
4.632	13	3.364	8	2.526	5	1.331	1
4.534	3						

[a] Copper Kα radiation, λ = 1.54178 Å; spinel ($MgAl_2O_4$), a_0 = 8.0831 Å, used as internal calibration standard.

studied; however, suitable preparations of these adducts were obtained for characterization. A major factor also complicating the study of this region was the rapid condensation of melamine to cyanuric acid and ammonia, especially at elevated temperature. Hydrolysis with the formation of ammonia and CO_2 also occurred at higher pH values, but was much slower. It is suggested that the hydrolysis rates for ammonia formation will be desired when practical application of the melamine–phosphoric acid processes is established.

The new adducts were characterized optically by polarizing light microscopy and by X-ray powder diffraction. Single-crystal data were determined for five of the adducts. The observed X-ray diffraction reflections were corrected by using silicon powder (NBS No. 640) or spinel as internal standards. The intensities were measured as peak heights above background and are expressed as percentages of the strongest line. Unit-cell parameters were determined from Weissenberg and precession photographs and were refined from the indexed powder diffraction patterns by least-squares computations. Because of the hygroscopic nature of $C_3H_6N_6 \cdot 4H_3PO_4$, its X-ray powder data were not obtained. The other adducts were relatively stable on exposure at ambient condition. The crystal data, as obtained by polarizing light microscopy (PLM), are given in Table II. The single-crystal data for five of the adducts are given in Table III; these data allow for calculations of the *hkl* spacings for the X-ray powder diffraction data given in Table IV. The X-ray powder data for the other compounds are shown in Table V.

The saturating melamine–H_3PO_4 adducts and the corresponding invariant point solutions containing two solid phases and a few univariant points for the system $C_3H_6N_6$–H_3PO_4–H_2O at 25 °C are given in Table VI. The data from 0–50% P_2O_5 are plotted in Figure 1, but more of the significant details between 0 and 0.9% P_2O_5 are shown in Figure 2. Two comparable analyses of each cell conducted two weeks apart confirmed that equilibrium had been obtained. Also, equilibrium was ascertained by the presence of well-developed euhedral crystals of each solid phase necessary to establish each invariant point and tie-line solution. Several duplicate samples of some invariant point compositions were obtained for additional confirmation.

Table VII lists the solid-phase identification and the saturating solution composition for the system $C_3H_6N_6$–NH_3–H_3PO_4–H_2O at 25 °C. These data are plotted in Figure 3. Since melamine is only slightly soluble in ammonium phosphate solutions, the phase system NH_3–H_3PO_4–H_2O reported by Lenfesty and Brosheer (*15*) serves as a boundary to establish the saturation fields for the melamine adducts.

Results and Discussion

Eleven melamine–phosphoric acid or ammonium phosphate adducts were isolated, formulated, and characterized by their unique optical and X-ray properties. Their phase relationships have been established at 25 °C. Crystal development and subsequent separation problems involved in WPA purification have been studied in other projects (*3*, *4*, *6*, *7*) and can now be described in relationship to the individual solid phases involved in each process.

Figure 3 shows the chemical parameters which control the reclamation of melamine from ammonium phosphate solutions. The ammonia system contains two adducts ($5C_3H_6N_6 \cdot 3H_3PO_4 \cdot 6H_2O$ and $C_3H_6N_6 \cdot NH_4H_2PO_4 \cdot 2H_2O$) completely surrounded by ammonium phosphate solutions; thus, these compositions will not be present in the $C_3H_6N_6$–H_3PO_4–H_2O system at 25 °C. The ammonium phosphate adduct has a more fundamental reason—the absence of ammonia. The shape of the isotherms in Figure 3 below 1% P_2O_5 is expected to be very

Table VI. System $C_3H_6N_6$-H_3PO_4-H_2O at 25 °C

sample no.	soln composn, wt % melamine	soln composn, wt % P_2O_5	pH	solid phase, optical microscopy
1	0.32	0.01	6.23	$C_3H_6N_6$
2	0.35	0.02	6.04	$C_3H_6N_6$ + $(C_3H_6N_6)_2{\cdot}H_3PO_4{\cdot}3H_2O$
3	0.18	0.03	5.47	$(C_3H_6N_6)_2{\cdot}H_3PO_4{\cdot}3H_2O$
4	0.16	0.07	4.39	$(C_3H_6N_6)_2{\cdot}H_3PO_4{\cdot}3H_2O$ + $(C_3H_6N_6)_3{\cdot}(H_3PO_4)_2{\cdot}4H_2O$
5	0.15	0.12	3.54	$(C_3H_6N_6)_3{\cdot}(H_3PO_4)_2{\cdot}4H_2O$ + $(C_3H_6N_6)_4{\cdot}(H_3PO_4)_3{\cdot}3H_2O$
6	0.16	0.14	3.28	$(C_3H_6N_6)_4{\cdot}(H_3PO_4)_3{\cdot}3H_2O$ + $(C_3H_6N_6)_6{\cdot}(H_3PO_4)_5{\cdot}4H_2O$
7	0.22	0.63	1.95	$(C_3H_6N_6)_6{\cdot}(H_3PO_4)_5{\cdot}4H_2O$ + $C_3H_6N_6{\cdot}H_3PO_4$
8	0.18	1.95	1.55	$C_3H_6N_6{\cdot}H_3PO_4$
9	0.18	10.01	0.93	$C_3H_6N_6{\cdot}H_3PO_4$
10	3.41	41.70	0.80	$C_3H_6N_6{\cdot}H_3PO_4$ + $C_3H_6N_6{\cdot}(H3PO_4)_2$ (A)
11			0.63	$C_3H_6N_6{\cdot}(H_3PO_4)_2$ (B)
12			0.63–0.8	$C_3H_6N_6{\cdot}(H_3PO_4)_2{\cdot}6H_2O$ (metastable)
13		59.00	<0.00	$C_3H_6N_6{\cdot}(H_3PO_4)_4$

Table VII. Phase System $C_3H_6N_6$-NH_3-H_3PO_4-H_2O at 25 °C

pH	soln composn, wt % NH_3-N	soln composn, wt % P_2O_5	soln composn, wt % Mel-N	solid phases[a]
9.77	4.27	3.82	0.28	Mel, TAP·3
8.57	8.93	21.96	0.06	Mel, TAP·3, DAP
7.52	8.72	22.64	0.07	Mel, DAP, Mel·MAP
7.38	3.77	10.15	0.18	Mel, Mel·MAP, 2:1·3
7.14	3.01	8.55	0.21	Mel, 2:1·3
7.01	2.08	5.56	0.26	Mel, 2:1·3
6.95	1.45	3.91	0.25	Mel, 2:1·3
6.09	3.86	13.29	0.04	5:3·6, 2:1·3, 3:2·4
6.08	2.99	10.35	0.04	3:2·4, 2:1·3
6.07	2.71	9.58	0.03	3:2·4, 2:1·3
6.06	4.71	15.82	0.03	5:3·6, 2:1·3
6.02	5.69	19.56	0.03	5:3·6, 2:1·3, Mel·MAP
6.02	9.80	34.52	0.04	Mel·MAP, MAP, DAP
5.74	6.75	23.75	0.02	5:3·6, 3:2·4
5.63	8.27	29.49	0.03	Mel·MAP, 3:2·4, MAP
5.60	7.98	28.48	0.02	Mel·MAP, 3:2·4, 5:3·6
5.56	4.41	16.86	0.03	5:3·6, 3:2·4
5.38	7.08	26.62	0.03	MAP, 3:2·4
4.92	5.42	21.89	0.04	MAP, 4:3·3, 3:2·4
4.63	4.50	19.72	0.03	MAP, 4:3·3
4.37	3.87	18.46	0.03	MAP, 4:3·3, 6:5·4
4.35	3.80	18.14	0.02	MAP, 4:3·3, 6:5·4
3.88	2.62	13.00	0.02	4:3·3, 3:2·4
3.78	3.21	16.06	0.02	4:3·3, 6:5·4
3.90	1.60	8.00	0.02	4:3·3, 3:2·4
3.67	1.08	5.34	0.03	4:3·3, 3:2·4
3.51	1.77	9.05	0.02	6:5·4, 4:3·3
3.28	3.47	18.18	0.02	6:5·4, 1:1, Mel·MAP
2.81	1.27	7.30	0.04	6:5·4, 1:1
1.77	3.78	25.06	0.16	MAP, 1:1

[a] Mel = melamine, $C_3H_6N_6$; TAP·3 = $(NH_4)_3PO_4{\cdot}3H_2O$; DAP = $(NH_4)_2HPO_4$; MAP = $NH_4H_2PO_4$; Mel·MAP = melamine·$NH_4H_2PO_4{\cdot}2H_2O$; 2:1·2 = 2melamine·$H_3PO_4{\cdot}3H_2O$; 3:2·4 = 3melamine·$2H_3PO_4{\cdot}4H_2O$; 5:3·6 = 5melamine·$3H_3PO_4{\cdot}6H_2O$; 4:3·3 = 4melamine·$3H_3PO_4{\cdot}3H_2O$; 6:5·4 = 6melamine·$5H_3PO_4{\cdot}4H_2O$; 1:1 = melamine·H_3PO_4.

complicated, somewhat similar to that in the acid system of Figure 2; i.e., the effect of a small quantity of ammonia on the isotherms of Figure 2 was not determined because the system would not be saturated with respect to ammonia and the data would not be applicable to either phase system being reported here. The basic data needed to develop a WPA purification and regeneration process are given. The solubility of melamine in the acid system at 10% P_2O_5 is sufficiently low to prevent a serious loss of melamine in the byproduct sludge fraction that will be formed after the major fraction of the phosphate has been removed.

Table VIII. pH versus Composition of Melamine Phosphate Adducts

pH	adduct	ratio Mel:H_3PO_4
0.4–0.5	Mel·$4H_3PO_4$	1.5:6
0.5–1.0	Mel·$2H_3PO_4$	3:6
1.0–3.3	Mel·H_3PO_4	6:6
2.8–4.4	6Mel·$5H_3PO_4{\cdot}4H_2O$	7.2:6
3.7–4.9	4Mel·$3H_3PO_4{\cdot}3H_2O$	8:6
4.9–5.6	3Mel·$2H_3PO_4{\cdot}4H_2O$	9:6
5.6–6.1	5Mel·$3H_3PO_4{\cdot}6H_2O$	10:6
6.1–7.4	2Mel·$H_3PO_4{\cdot}3H_2O$	12:6

A comparative summary of the melamine–phosphoric acid adducts, along with the pH range of their stability fields, is shown in Table VIII. Other ratios may exist at other temperatures.

Registry No. H_3PO_4, 7664-38-2; NH_3, 7664-41-7; melamine, 108-78-1.

Literature Cited

(1) Bann, B.; Miller, S. A. *Chem. Rev.* **1958** *58*, 131–172.
(2) Frazier, A. W.; Gautney, J.; Cabler, J. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1982** *21*, 470–473.
(3) Sheridan, R. C. U.S. Patent 3 920 796, Nov 18, 1975.
(4) Kohler, J. J.; Gautney, J.; Kim, Y. K.; McCullough, J. F. U.S. Patent 4 139 597, Feb 13, 1979.
(5) Gautney, J.; Frazier, A. W.; Kim, Y. K.; Hatfield, J. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1982** *21*, 464–470.
(6) Sheridan, R. C.; McCullough, J. F. U.S. Patent 4 239 739, Dec 16, 1980.
(7) McCullough, J. F.; Sheridan, R. C. U.S. Patent 4 017 589, Apr 12, 1977.
(8) Volfkovic, V.S.I.; Feldmann, W.; Kozmina, M. L. *Z. Anorg. Allg. Chem.* **1979** *457*, 20–30.
(9) Frazier, A. W.; Scheib, R. M.; Thrasher, R. D. *J. Agric. Food Chem.* **1972** *20*, 138–145.
(10) Konishi, K.; Imaniski, A. *Nippon Dojahiryagaku Zasshi* **1941** *15*, 559–574.
(11) Scholl, W.; Davis, R. O. E.; Brown, B. E.; Reid, F. R. *Ind. Eng. Chem.* **1937** *29*, 202–205.
(12) Vol'fkovich, S. I.; Zusser, E. E.; Remen, R. E. *Bull. Acad. Sci. URSS, Cl. Sci. Chim.* **1946**, 571–579.
(13) Van Wazer, J. R. *Phosphorus and Its Compounds*; Interscience: New York, 1961; pp 997–1069.
(14) Winchell, A. N. *The Optical Properties of Organic Compounds*; University of Wisconsin Press: Madison, WI, 1943.
(15) Lenfesty, F. A.; Brosheer, J. C. *J. Chem. Eng. Data* **1960**, *5*, 152–154.

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