the importance of adequate conservation measures for blood, grease, etc. (Steffen, 1970), in order to minimize the *pro rata* fee for discharging untreated abattoir effluent into municipal sewers.

The Hemoglobin–Fe Interaction. The negative charges on hemoglobin above its isoelectric pH (6.6–6.8) were responsible for its migration toward the anode during electrophoresis in borate buffer at pH 9.2. The gradual addition of Fe(III) would be expected to neutralize these charges electrokinetically. Indeed, $Fe_2(SO_4)_3$ completely immobilized hemoglobin in the electrophoretic field. Moreover, the accumulation of Fe in effluent by equilibrium dialysis (Table III), and the elimination of the heme bands at 572 and 538 nm from the hemoglobin spectrum were interpreted as a complexation reaction (Hughes and Klotz, 1956) between Fe(III) and hemoglobin. The ratio of COD of dialysate to milligrams per liter of accumulated $Fe_2(SO_4)_3$ was 1.6.

Uncertainties in the settling property of the coagulum, depending on the holding interval before addition of base, may be explained by the nature of the nonequilibrium, polynuclear Fe species (American Water Works Association, 1971) whose molecular weight and, hence, charge density (Jirgensons and Straumanis, 1962) would be expected to increase with time. Under equilibrium conditions, COD would also be reduced by occlusion and entrainment of effluent solute within the depositing hydroxide.

The Importance of Base. The addition of $Fe_2(SO_4)_3$ changed the effluent pH from 7.3 to 2.9, thereby creating a state of high colloid concentration–low alkalinity, which requires treatment based only on one parameter, *viz.* coagulant dosage (Weber, 1972). However, it was necessary to restore the alkalinity, in order to effect phase separation and, consequently, COD reduction. Since in a strongly basic medium, the positive charge on metal sols is reversed (Blaedel and Meloche, 1963) the alkalinity should not exceed the maximum of 9.6, below which the biggest reduction in COD was obtained. Thus, the high COD remaining in effluent after adjustment to pH 11.6 (Table I, no. 12) may be attributed to stabilization of the solute phase by repulsion of negative charges.

Coagulation of solute in abattoir effluent with metal salts may therefore be viewed as a practicable method of reducing the oxygen demand in abattoir effluent, once the mechanism is understood to be chemical in nature, depending on pH, time, and the ratio of concentration of the reactants.

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Conditions Affecting the Purification of Simulated Wet-Process Phosphoric Acids by Solvent Extraction

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Eight organic solvents—methyl ethyl ketone, 1-butanol, 1-heptanol, 2-methyl-1-propanol, 1-pentanol, *tert*-pentanol, tri-*n*-butyl phosphate, and isophorone—that had been selected from some 40 solvents in a previous screening test were tested for their effectiveness in separating the impurities from simulated wet-process phosphoric acids containing 35–75% H_3PO_4. The first three solvents listed were promising enough for more intensive tests. Methyl ethyl ketone and 1-butanol were the most effective extractants of P_2O_5; 1-heptanol was less effective, but its insolubility in aqueous media was a distinct advantage in its recovery for recycle. Purification of the acid was increased, with some loss in extraction of P_2O_5, by partial ammoniation to a mole ratio $NH_3:H_3PO_4$ of 0.1, with which 70% of the P_2O_5 was extracted with only 20% of the metallic impurities. The excellent behavior of methyl ethyl ketone led to a study of the use of acetone for the purification of wet-process acid. With partial ammoniation acetone extracted 85% of the P_2O_5 and only 20% of the metallic impurities, and the acetone was readily recovered by distillation.

Interest in the purification of wet-process phosphoric acid has increased in recent years because of the increased costs of providing electric-furnace phosphoric acid. Purification is necessary for use in food products and in certain fertilizer applications, particularly liquid fertilizers. The

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solvent extraction process is one of the promising methods for separating the acid from its impurities (Blumberg, 1971; Slack, 1968). The objective of this study is to determine the effects of composition parameters of simulated wet-process acids on the solvent extraction of the acid and the separation of the various impurities in 1:1 weight ratios of solvent to acid mixtures.

A considerable number of solvents has been studied as extractants of wet-process phosphoric acid, including alco-

Table I

Factor	Min	Max
Composition, wt %		
Fe₂O₃ + Al₂O₃	1	3
MgO	0.2	1.0
SO₃ + F	1	5
H₃PO₄	35	75
Mole ratio NH₃:H₃PO₄	0	0.3

Table I

Factor	Min	Max
Composition, wt %		
Fe_2O_3 + Al_2O_3	1	3
MgO	0.2	1.0
SO_3 + F	1	5
H_3PO_4	35	75
Mole ratio NH_3:H_3PO_4	0	0.3

Table II. Commercial Wet-Process Phosphoric Acids

	Composition, wt %					
Acid	H_3PO_4	Fe_2O_3	Al_2O_3	MgO	SO_3	F
Green[a]	75.8	1.37	0.67	0.96	1.82	1.10
Black[b]	75.1	1.02	1.87	0.55	2.50	1.03

[a] Prepared from calcined North Carolina phosphate rock. [b] Prepared from uncalcined Florida phosphate rock.

Table III. Compositions of Simulated Wet-Process Phosphoric Acids

No.	Composition, wt %						Mole ratio NH_3:H_3PO_4
	H_3PO_4	Fe_2O_3	Al_2O_3	MgO	SO_3	F	
1	65	0.75	0.75	0.4	1.4	0.6	0
2	45	1.25	1.25	0.4	1.4	0.6	0
3	45	0.75	0.75	0.8	1.4	0.6	0
4	65	1.25	1.25	0.8	1.4	0.6	0
5	45	0.75	0.75	0.4	2.8	1.2	0
6	65	1.25	1.25	0.4	2.8	1.2	0
7	65	0.75	0.75	0.8	2.8	1.2	0
8	45	1.25	1.25	0.8	2.8	1.2	0
9	45	0.75	0.75	0.4	1.4	0.6	0.2
10	65	1.25	1.25	0.4	1.4	0.6	0.2
11	65	0.75	0.75	0.8	1.4	0.6	0.2
12	45	1.25	1.25	0.8	1.4	0.6	0.2
13	65	0.75	0.75	0.4	2.8	1.2	0.2
14	45	1.25	1.25	0.4	2.8	1.2	0.2
15	45	0.75	0.75	0.8	2.8	1.2	0.2
16	65	1.25	1.25	0.8	2.8	1.2	0.2
17	55	1.50	1.50	0.6	2.1	0.9	0.1
18	55	0.50	0.50	0.6	2.1	0.9	0.1
19	55	1.0	1.0	1.0	2.1	0.9	0.1
20	55	1.0	1.0	0.2	2.1	0.9	0.1
21	55	1.0	1.0	0.6	3.5	1.5	0.1
22	55	1.0	1.0	0.6	0.7	0.3	0.1
23	55	1.0	1.0	0.6	2.1	0.9	0.3
24	55	1.0	1.0	0.6	2.1	0.9	0
25	75	1.0	1.0	0.6	2.1	0.9	0.1
26	35	1.0	1.0	0.6	2.1	0.9	0.1
27–30	55	1.0	1.0	0.6	2.1	0.9	0.1

hols (Amanrich, 1971; Bekturov et al., 1969; Frankenfeld and Goetzmann, 1972c; Krupatkin and Stepanova, 1970; Moldovan and Mann, 1964; Mal'tseva et al., 1969; Montecatini Edison, 1968; Ohira, 1962; Sabaev and Shokin, 1963; Sabaev et al., 1964; Thompson and Worthington, 1971), esters (Amanrich, 1971; Bekturov et al., 1969), ethers (Krupatkin and Shcherbakova, 1971; Muldagaliev and Tanasheva, 1970), ketones (Bekturov et al., 1969; Frankenfeld and Goetzmann, 1972a; Moldovan and Mann, 1964), amines (Canadian Industries, Ltd., 1964; Hazen and Henrickson, 1967; Koerner and Saunders, 1964; Ricci et al., 1970; Sato, 1965), and amides (Baniel and Blumberg, 1964). In a previous unpublished TVA study some 40 promising solvents were screened as extractants of wet-process acid, and the nine most promising solvents were selected for detailed study as extractants of simulated acids. One of the solvents, isopropyl ether, was dropped from the study when it was found to be effective only with acids containing at least 75% H_3PO_4. Among the variables studied was partial ammoniation of the acid before extraction, a procedure that had been investigated by others (Frankenfeld and Goetzmann, 1972b,c; Pulverfabrik Skodawerk-Wetzler A. G., 1937; Westphal and Wegmann, 1953).

EXPERIMENTAL CONDITIONS

The extraction tests were made with simulated wet-process acids prepared from reagent chemicals to contain 35–75% H_3PO_4 and the desired amounts of the different impurities. The experimental design was intended to show the effects of the amounts of impurities, partial neutralization of the acid with ammonia, and concentration of acid on the separation of the acid from its impurities by each solvent at room temperature. The ranges of these factors are shown in Table I. Commercial wet-process acids—a green acid made from calcined North Carolina phosphate rock and a black acid made from uncalcined Florida phosphate rock—were used instead of simulated acids for the acetone extractions. The compositions of these acids are shown in Table II.

In each test with simulated acids a mixture of 100 g of the acid and 100 g of the solvent was stirred vigorously for 20 min in a 400-ml beaker, after which the mixture was transferred to a separatory funnel and allowed to settle for 20 min. The aqueous and organic phases were separated, their weights and volumes were determined, and samples

of the aqueous phases were analyzed. The experimental conditions of the tests with each solvent are summarized in Table III. The order in which the tests were made was determined by use of a table of random numbers, which minimized the interference of any unknown variables with the effects of the variables under study.

In the stripping of the acid from the organic phase after the extraction, the extracted acid was recovered by stripping in four steps with distilled water. The amounts of water used in the successive steps were 10, 50, 100, and 150 ml per 100 g of initial acid. In each step, the organic phase and water were mixed thoroughly and then allowed to settle for 10 min in a separatory funnel, after which the phases were separated. The dilute acids stripped from each step were weighed and analyzed for P_2O_5 and solvents.

RESULTS

The experimental design of the study of extraction by each solvent was the Box central composite design in five variables (Box and Wilson, 1951). To decrease the number of variables in Table III to a more manageable five, Fe_2O_3 and Al_2O_3 were combined into the single variable R_2O_3 with the weight ratio Fe_2O_3:Al_2O_3 maintained at unity, and SO_3 and F were combined into a single anion impurity with the weight ratio SO_3:F maintained at 7:3. These ratios are not constant in commercial acids, but the interactions between Fe_2O_3 and Al_2O_3 and between SO_3 and F were expected to have no significant effect on the separation of the impurities from the acids by solvent extraction. The design variables x_1 through x_5 were related to the composition of the acid by the following expressions in which the formulas denote the concentration, weight per cent, of the component of the acid: $R_2O_3 = 2.0 + 0.5x_1$

Table IV. Extraction of Simulated Wet-Process Acids with Organic Solvents; Extraction with 1-Butanol

No.	Fraction, %, of component extracted							Distribution coefficient						
	P_2O_5	Fe_2O_3	Al_2O_3	MgO	SO_3	F	NH_3	P_2O_5	Fe_2O_3	Al_2O_3	MgO	SO_3	F	NH_3
1	93.3	75.3	52.5	52.9	86.4	59.3		0.468	0.103	0.037	0.038	0.215	0.049	
2	52.1	0.3	8.3	2.7	40.3	17.6		0.270	0.001	0.022	0.007	0.167	0.053	
3	55.5	6.2	3.4	52.8	39.2	21.0		0.300	0.016	0.009	0.270	0.155	0.064	
4	80.5	44.3	24.2	27.7	65.0	30.4		0.394	0.076	0.030	0.037	0.178	0.042	
5	80.2	34.4	0.0	12.7	78.2	30.1		0.427	0.055	0.000	0.015	0.380	0.046	
6	84.7	80.5	53.0	31.5	83.7	44.8		0.960	0.718	0.196	0.080	0.890	0.141	
7	47.9	39.0	12.6	29.8	48.4	30.7		0.985	0.686	0.155	0.456	1.006	0.475	
8	59.3	15.0	3.0	4.2	44.1	15.9		0.322	0.039	0.007	0.010	0.174	0.042	
9	33.8	1.2	0.0	9.1	11.8	10.8	2.5	0.178	0.004	0.000	0.035	0.047	0.042	0.009
10	46.8	6.6	15.4	3.7	15.0	6.1	4.4	0.216	0.017	0.045	0.009	0.043	0.016	0.011
11	48.2	3.6	0.0	3.2	16.9	7.7	4.8	0.232	0.009	0.000	0.008	0.051	0.021	0.013
12	23.5	0.0	2.7	2.1	6.2	10.5	0.0	0.116	0.000	0.011	0.008	0.025	0.044	0.000
13	59.3	2.0	0.0	3.5	30.4	15.1	9.9	0.284	0.004	0.000	0.007	0.085	0.035	0.021
14	38.6	0.0	1.2	1.4	20.5	9.1	3.2	0.202	0.000	0.004	0.005	0.083	0.032	0.011
15	38.2	3.2	0.0	3.4	14.1	13.8	1.9	0.206	0.011	0.000	0.012	0.054	0.053	0.006
16	54.1	0.0	0.0	7.6	21.9	6.9	6.5	0.250	0.000	0.000	0.017	0.059	0.016	0.015
17	52.7	4.6	0.0	3.2	29.3	9.7	5.4	0.254	0.011	0.000	0.008	0.095	0.024	0.013
18	66.0	9.1	0.0	6.5	44.3	14.0	16.0	0.334	0.017	0.000	0.012	0.137	0.028	0.033
19	54.6	2.3	0.0	7.5	24.9	13.2	6.3	0.271	0.005	0.000	0.018	0.074	0.034	0.015
20	60.9	12.0	11.1	1.2	37.6	14.2	9.2	0.302	0.026	0.024	0.002	0.117	0.032	0.020
21	68.8	12.2	0.0	0.7	52.3	14.0	13.1	0.347	0.022	0.000	0.001	0.172	0.026	0.024
22	46.5	0.1	0.0	5.3	13.1	17.7	4.9	0.229	0.000	0.000	0.015	0.040	0.057	0.014
23	31.7	0.0	0.0	3.0	7.7	8.5	1.3	0.156	0.000	0.000	0.010	0.028	0.031	0.004
24	76.1	13.4	19.6	16.0	59.9	24.7		0.398	0.028	0.030	0.024	0.186	0.041	
25	78.0	20.0	13.7	15.1	53.7	12.3	23.8	0.231	0.016	0.010	0.012	0.076	0.009	0.020
26	34.7	7.8	0.0	3.0	17.8	13.8	3.0	0.193	0.031	0.000	0.011	0.079	0.058	0.011
27	59.2	3.5	1.0	8.2	37.3	8.2	8.0	0.297	0.019	0.002	0.018	0.122	0.018	0.018
28	57.0	3.9	0.0	5.7	32.1	16.5	7.9	0.280	0.008	0.000	0.013	0.100	0.042	0.018
29	57.3	0.0	5.1	8.8	31.3	14.0	7.7	0.286	0.000	0.012	0.021	0.097	0.035	0.018
30	57.2	3.3	2.8	4.4	28.0	19.0	8.3	0.284	0.007	0.006	0.010	0.083	0.050	0.019

($Al_2O_3 = Fe_2O_3 = 1.0 + 0.25x_1$); MgO $= 0.6 + 0.2x_2$; anion impurity $= 3.0 + 1.0x_3$ ($SO_3 = 2.1 + 0.7x_3$; F $= 0.9 + 0.3x_3$); mole ratio $NH_3:H_3PO_4 = 0.1 + 0.1x_4$; $H_3PO_4 = 55 + 10x_5$. The x's are coded forms of the variables that range from -2 to $+2$ except for x_4 which ranges from -1 to $+2$.

The measured responses from the extraction by each solvent included E_i, the fraction, per cent, of each component extracted from the aqueous to the organic phase; D_i, the distribution coefficient of each component between the organic and aqueous phases, defined as

$$D_i = \lceil C_i \rceil_o / \lceil C_i \rceil_a = \lceil E_i / (100 - E_i) \rceil (V_a / V_o) \quad (1)$$

The subscript i refers to Fe_2O_3, Al_2O_3, MgO, SO_3, F, NH_3, or P_2O_5; the subscripts a and o refer to the aqueous and organic phases, respectively; V is the volume of the separated phase after the extraction. The representative experimental results are shown in Table IV.

The data for each solvent were analyzed by regression of the expression

$$y = b_0 + \sum_1^5 b_i x_i + \sum_1^5 b_{ii} x_i^2 + \sum_1^5 b_{ij} x_i x_j$$
$$(i < j \le 5) \quad (2)$$

where y is an observed response, such as the extraction of any constituent, E_i; D_i is the distribution coefficient; and the b's are empirical constants. The values of the b's for each response for the three most promising solvents are listed in Table V, and from these the responses were cal-culated for different experimental conditions; examples of these calculated results are shown in Table VI and plotted in Figures 1, 2, and 3. Almost all the correlation coefficients were 0.95 or higher, and the standard deviation of the amount extracted, observed $vs.$ calculated, is of the same order of magnitude as that associated with the four replicated runs, 27–30, for each solvent.

The factors that have the greatest effects on the extraction of P_2O_5 are the initial concentration of P_2O_5, the degree of ammoniation, and the concentration of anion impurity, SO_3 + F. In general, the extraction and the distribution coefficient of P_2O_5 increased with an increase in the initial P_2O_5 concentration.

The order of extractability of the P_2O_5 by each solvent was methyl ethyl ketone > 1-butanol > $tert$-pentanol > 2-methyl-1-propanol > tri-n-butyl phosphate > isophorone > 1-pentanol > 1-heptanol (Figure 1). The separation of the impurities from the partially ammoniated acid was good, and phase separation was fast for most of the solvents.

Increase in the anion impurity increased the extraction of P_2O_5 slightly, but also increased the extraction of the metallic impurities. Addition of ammonia increased the separation of the impurities, but decreased considerably the amount of P_2O_5 extracted (Figures 2 and 3). If the objective is to produce a pure acid, H_3PO_4 solution, the addition of ammonia may require further study to remove the NH_3 from the organic layer; if the objective is to prepare liquid fertilizers containing ammonium phosphates, the addition of ammonia will not be detrimental to the product. A reasonable compromise on acid purity and per cent extracted was obtained by ammoniation to a mole

Table V. Empirical Constants for Use in Equation 2

Con-stant	Fraction, %, of component extracted							
	P_2O_5	Fe_2O_3	Al_2O_3	MgO	SO_3	F	NH_3	$D_{P_2O_5}$
				Extraction with 1-Butanol				
b_0	58.96	1.47	1.92	4.34	32.37	12.96	8.87	0.261
b_1	− 1.81	−1.14	1.63	−3.88	−2.45	−2.32	−1.09	−0.021
b_2	−3.92	−4.52	−4.44	1.08	−5.66	−2.42	−0.53	−0.011
b_3	3.06	2.53	−1.53	−2.88	5.78	−0.18	1.09	0.071
b_4	−13.34	−17.01	−9.34	−11.36	−21.85	−10.64	2.80	−0.151
b_5	9.17	8.97	6.94	3.98	7.71	2.89	2.48	0.077
b_{11}	−0.14	1.77	−0.04	0.79	1.11	0.09	−0.14	0.014
b_{22}	−0.54	1.84	1.35	0.66	−0.30	0.56	−0.88	0.012
b_{33}	−0.56	1.59	−0.04	0.32	0.07	1.11	−0.56	0.013
b_{44}	−0.36	8.44	5.27	6.28	4.79	4.73	−4.58	0.057
b_{55}	−0.90	3.53	1.67	1.83	0.84	0.40	0.53	−0.006
b_{12}	4.50	2.06	−0.72	−0.55	4.14	1.77	0.28	−0.058
b_{13}	2.44	3.25	3.13	4.83	1.67	1.34	0.05	0.001
b_{14}	−1.03	0.71	−0.04	4.85	0.60	1.09	−0.31	0.007
b_{15}	3.22	2.57	0.98	3.04	2.24	−0.13	−0.17	0.003
b_{23}	−2.80	−1.89	0.45	−1.35	−3.63	−0.48	−0.17	−0.001
b_{24}	3.29	5.18	3.55	−1.01	4.58	3.22	−0.43	0.003
b_{25}	−1.58	−4.13	−5.24	−3.74	−1.01	−2.69	0.05	0.004
b_{34}	2.96	−3.06	0.18	3.48	0.85	1.04	0.61	−0.066
b_{35}	−4.64	−3.33	−1.01	1.87	−3.64	−0.94	0.28	0.055
b_{45}	0.95	−10.97	−7.26	−4.22	−3.14	−5.56	1.13	−0.075
S	5.20	8.49	6.07	6.07	6.25	6.03	5.12	0.100
R	0.985	0.974	0.970	0.970	0.987	0.957	0.860	0.957
				Extraction with 1-Heptanol				
b_0	27.01	1.29	−0.11	3.79	11.96	6.96	1.23	0.153
b_1	−1.37	−0.51	−0.12	−2.64	−2.52	0.00	−0.13	−0.009
b_2	−0.67	−0.67	−0.17	1.88	−1.94	−3.07	−0.26	−0.003
b_3	3.60	0.96	−1.35	−2.58	4.88	−0.87	0.15	0.020
b_4	−7.64	−1.60	−0.91	−2.46	−10.16	−0.90	0.77	−0.043
b_5	12.06	4.55	0.11	−1.74	9.59	3.33	0.99	0.055
b_{11}	−0.34	−0.37	0.25	0.12	0.70	0.83	−0.25	−0.002
b_{22}	−0.18	0.58	0.32	−0.19	−0.01	1.57	−0.14	−0.001
b_{33}	−0.09	0.07	0.25	−0.04	0.39	0.80	−0.11	−0.001
b_{44}	0.47	0.19	1.03	1.97	3.94	1.57	−0.69	0.003
b_{55}	1.41	2.53	0.58	0.58	2.66	0.77	0.82	0.002
b_{12}	−0.42	−2.04	−2.37	−2.83	0.10	−0.42	0.16	−0.003
b_{13}	0.24	−0.42	0.90	3.62	−0.90	−2.18	−0.29	0.001
b_{14}	0.17	0.28	1.66	3.28	−1.18	0.24	−0.08	0.001
b_{15}	−0.19	−0.77	2.74	3.63	−2.20	2.29	−0.15	−0.002
b_{23}	0.76	0.27	−0.53	−2.38	−1.15	2.24	−0.15	0.005
b_{24}	−0.85	−0.27	−2.02	−3.48	−0.70	−1.69	−0.44	−0.006
b_{25}	−0.06	−0.19	−2.37	−3.08	0.16	−1.25	−0.29	0.000
b_{34}	−0.12	−2.17	−0.19	2.45	−0.55	−1.35	0.19	−0.001
b_{35}	0.41	1.14	0.90	4.21	3.20	−0.08	0.16	0.000
b_{45}	−2.82	−2.20	1.66	2.85	−6.68	0.52	0.30	−0.012
S	1.22	2.77	2.23	5.11	4.00	4.75	1.69	0.009
R	0.999	0.968	0.963	0.953	0.989	0.911	0.861	0.997
				Extraction with Methyl Ethyl Ketone				
b_0	69.46	4.74	2.44	7.53	31.34	17.01	14.77	0.309
b_1	−1.12	−2.52	−2.18	−5.93	0.50	−2.61	−1.72	−0.033
b_2	−4.06	−4.27	−3.95	−0.88	−5.36	−5.89	−1.12	0.013
b_3	3.56	0.61	−1.38	−2.37	2.82	0.04	1.38	0.057
b_4	−17.81	−25.82	−20.66	−19.62	−25.88	−16.41	3.45	−0.154
b_5	8.73	7.98	6.02	4.38	8.22	3.16	2.85	0.057
b_{11}	0.10	2.31	1.92	1.26	1.16	0.83	0.07	0.011
b_{22}	−0.20	2.28	2.20	0.78	−0.11	0.90	−0.75	0.008
b_{33}	−1.04	1.80	0.21	0.44	−1.01	1.52	−1.26	0.005

Table V *(Continued)*

Con-stant	Fraction, %, of component extracted							
	P_2O_5	Fe_2O_3	Al_2O_3	MgO	SO_3	F	NH_3	$D_{P_2O_5}$
b_{44}	-1.48	14.54	11.45	9.61	6.59	8.39	-7.41	0.041
b_{55}	-3.38	0.16	1.77	1.30	-1.68	0.23	-1.47	-0.006
b_{12}	3.16	0.27	-2.77	0.75	-1.45	0.02	0.41	-0.031
b_{13}	3.90	4.98	3.22	4.42	5.46	-1.82	0.04	-0.013
b_{14}	-2.60	-0.33	6.23	7.36	-4.44	4.66	-0.27	0.021
b_{15}	3.11	0.27	1.98	1.75	-3.42	2.45	-0.33	-0.026
b_{23}	-2.80	-3.54	-0.15	0.22	1.20	3.52	-0.33	0.028
b_{24}	2.54	7.47	2.08	0.47	2.40	2.40	-0.36	-0.035
b_{25}	-2.91	-1.71	-4.94	-2.79	-5.04	-2.51	0.04	0.018
b_{34}	4.86	-3.41	0.16	2.99	5.02	-2.74	0.77	-0.035
b_{35}	-4.37	-4.49	1.09	1.43	1.26	-2.52	0.41	0.024
b_{45}	4.80	-7.84	-5.83	-4.48	-4.95	-1.49	1.53	-0.034
S	6.51	12.87	8.16	7.39	10.92	9.70	7.35	0.060
R	0.984	0.962	0.976	0.978	0.971	0.949	0.863	0.979

Table VI. Calculated Data for Simulated Acids and Experimental Data for Commercial Acids

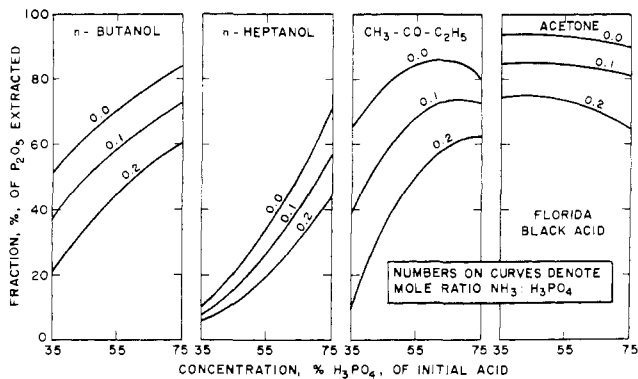|	Initial acid			Fraction, %, of						
	Concn, %	Mole ratio	P_2O_5		Component rejected					
Solvent	H_3PO_4	NH_3:H_3PO_4	extd.	Fe_2O_3	Al_2O_3	MgO	SO_3	F	NH_3	
			Tests with Simulated Acids[a]							
1-Butanol	45	0.0	63	83	94	75	22	68		
		0.1	49	100	100	95	48	78	86	
		0.2	34	100	100	96	68	70	88	
	65	0.0	78	36	59	60	9	53		
		0.1	67	79	84	85	39	76	82	
		0.2	56	100	100	98	63	91	80	
1-Heptanol	45	0.0	22	100	72	38	43	66		
		0.1	16	100	98	63	69	73	93	
		0.2	12	100	100	77	55	62	93	
	65	0.0	51	76	98	92	12	75		
		0.1	40	80	98	94	40	63	93	
		0.2	30	84	92	84	62	60	89	
Methyl ethyl ketone	45	0.0	79	63	69	63	38	52		
		0.1	57	100	100	92	62	75	82	
		0.2	33	100	100	100	79	78	87	
	65	0.0	86	29	44	46	12	46		
		0.1	75	83	86	82	50	73	78	
		0.2	60	100	100	100	77	82	77	
			Tests with Green Commercial Acid[b]							
Acetone[c]	45	0.0	95	44	58	41	25	25		
		0.1	85	82	83	81	64	41	59	
		0.2	71	98	96	94	83	56	72	
	65	0.0	95	32	50	35	16	25		
		0.1	85	80	75	75	64	46	61	
		0.2	70	98	89	91	89	66	74	
			Tests with Black Commercial Acid[d]							
Acetone[c]	45	0.0	94	38	60	60	41	65		
		0.1	85	87	75	77	46	74	60	
		0.2	75	84	87	88	68	79	66	
	65	0.0	92	28	44	60	9	70		
		0.1	83	84	69	82	54	87	67	
		0.2	70	87	90	91	75	89	77	

[a] Initial acid contained Fe_2O_3, 1.0; Al_2O_3, 1.0; MgO, 0.6; SO_3, 2.1; and F, 0.9%. [b] Acid prepared from calcined North Carolina phosphate rock, Table II. [c] Weight ratio acetone to initial acid = 2. [d] Acid prepared from uncalcined Florida phosphate rock, Table II.
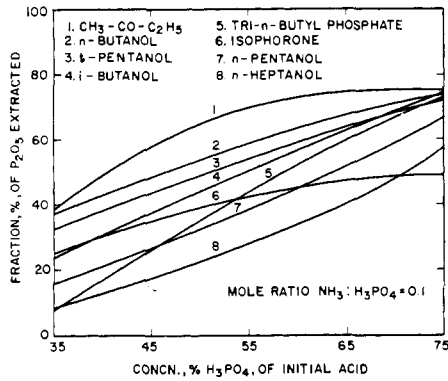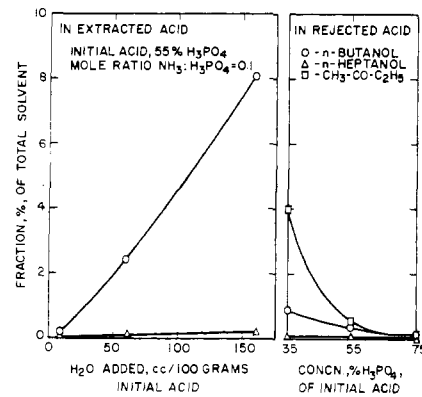
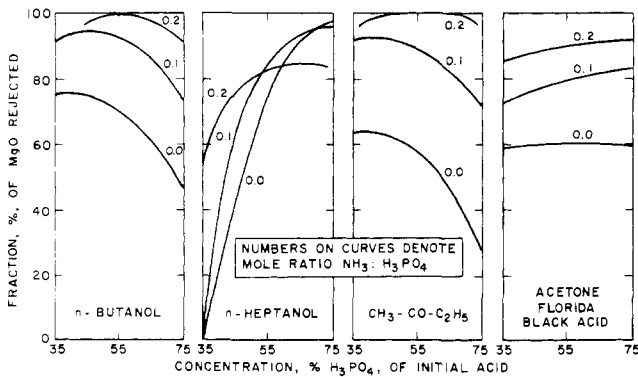**Figure 1.** Extraction of phosphoric acid from simulated wet-process acids.

Figure 2. Effect of partial ammoniation on extraction of phosphoric acid from wet-process acids.

Figure 3. Separation of magnesium by extraction of wet-process acids.

Figure 4. Stripping of phosphoric acid from organic solvent extracts of wet-process acids.

Figure 5. Loss of solvent in extraction of wet-process acids and stripping of extracts.

ratio $NH_3:H_3PO_4$ of about 0.1; a higher ratio may be required if the purity of the extracted acid is more important than the amount of acid extracted. The ranges of the impurities tested in this study were wide enough to cover wet-process phosphoric acids made from most known commercial phosphate deposits in the world, and the predictions made for these solvents have a wide application.

In tests of the recovery of the H_3PO_4 from 1-butanol and 1-heptanol extracts (Figure 4) excellent stripping efficiency was obtained in four stripping steps. Neither the initial acid concentration nor the presence of NH_3 in the initial acid had much effect on the stripping steps. Stripping from 1-heptanol was more effective than from 1-butanol, and the amount of water required for stripping the acid from 1-heptanol was less than that required for 1-butanol. The phase separation in the stripping steps was fast and sharp with both solvents.

The dilution of the product acid can be minimized by countercurrent stripping, and the concentration of the product acid extracted by either alcohol can be as high as 75% of the initial acid concentration.

The solvent contents of the purified acid and the residual impure acid phase were measured for both alcohols (Figure 5). Neither the degree of ammoniation nor the initial acid concentration had any significant effect on the amount of alcohol in the purified acid, but the loss of solvent in the impure acid phase decreased with an increase in the initial acid concentration. The solubility of 1-heptanol in the acid solution is so low that it may not be necessary to recover the solvent from the product at all, but the dissolved 1-butanol may have to be recovered from the product acid.

TESTS WITH WATER-MISCIBLE SOLVENTS

Evaluation of the eight screened solvents showed methyl ethyl ketone to be the most promising for the purification of the simulated acid. Methyl ethyl ketone is miscible with water, however, and it would have to be recovered by distillation; it boils at 79.6°. Acetone is the lowest molecular weight ketone, has the lowest boiling point (56.2°), and is commercially available. The extraction with acetone was evaluated for the purification of two commercial wet-process phosphoric acids—a green acid made from calcined North Carolina rock and a black acid made from uncalcined Florida rock (Table II). In this series of tests a 100-g batch of acid was stirred in an open 600-ml beaker for 5 min with either 100 or 200 g of acetone. The separation of phases and treatment of the separates were the same as with other solvents. Volume changes during extraction with acetone varied between 5 and 10%; these changes are important in process design,
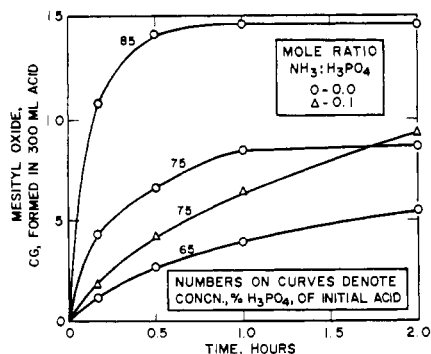
Figure 6. Formation of mesityl oxide at 89° in mixtures of acetone and phosphoric acid.
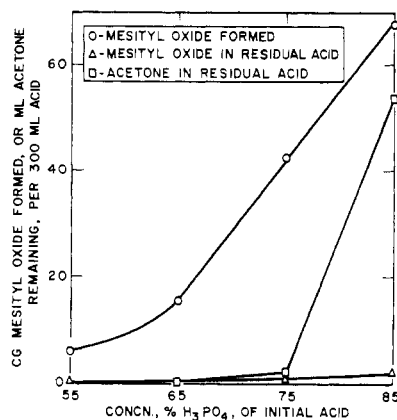

Figure 7. Distillation of acetone from its mixtures with phosphoric acid.

but their effects would be minimized in a continuous process.

Results of acetone extractions of the two commercial wet-process phosphoric acids are listed at the bottom of Table VI. An increase in the weight ratio of acetone to initial acid solution from 1 to 2 increased slightly the fraction of the acid extracted, but did not change the separation of the impurities significantly. Acetone extracted H_3PO_4 from the commercial wet-process acids better than did the methyl ethyl ketone, and the acetone separated the impurities very well also.

RECOVERY OF ACETONE

Acetone undergoes acid-catalyzed dehydration and polymerization in concentrated H_2SO_4 to mesityl oxide [$(CH_3)_2C$=$CHCOCH_3$], phorone [$(CH_3)_2$=$CHCOCH$=$(CH_3)_2$], or mesitylene [$(CH_3)_3C_6H_3$], depending upon the imposed conditions (Noller, 1957). In separating acetone from H_3PO_4, mesityl oxide probably will be the major decomposition product because the acidity and dehydration power of H_3PO_4 are lower than those of H_2SO_4.

Mesityl oxide has a strong absorption peak at 243 nm, and its molar extinction coefficient, ϵ, is 1.14×10^4, whereas acetone has a rather weak absorption peak at 265 nm (ϵ 17.6). Thus, the formation of mesityl oxide during distillation of acetone either alone or from its mixture with phosphoric acid was measured by a Cary 17 spectrophotometer.

The polymerization of acetone was studied under reflux conditions by placing 300 ml of reagent grade acid in a distilling flask, heating in an oil bath to 90°, and adding 50 ml of acetone through the sample port. The temperature of the mixture remained fairly constant at about 89° throughout the subsequent 2-hr refluxing.

The major factors that affect polymerization of the ace-

tone are the duration of the distillation and the initial concentration of the phosphoric acid (Figure 6). Almost all water goes into the acetone phase. The amount of mesityl oxide increased with an increase in time of heating and with an increase in initial acid concentration. Partial neutralization with ammonia to a mole ratio $NH_3:H_3PO_4$ of 0.1 decreased the formation of mesityl oxide in the early stage, but after 2 hr there was little difference in the amounts of mesityl oxide in the ammoniated and unammoniated samples. At 110° there was no difference in the rate of formation of mesityl oxide in the presence of 75 or 85% H_3PO_4.

The acetone was distilled from a 1-l. flask, to which was attached a 15-cm fractionation column. To the flask was added 300 ml of acid and 600 ml of acetone, and each mixture with different initial concentrations of H_3PO_4 was distilled in an oil bath at 150°. The condensates were collected in fractions at successive boiling points, and each fraction was analyzed for acetone and mesityl oxide.

Most of the acetone distilled off before the temperature of the solution rose to 100°, and the distillate then contained no measurable amount of mesityl oxide. When the temperature of the solution reached 145°, the distillation was stopped and the residue was cooled and analyzed for mesityl oxide and acetone.

The formation of mesityl oxide increased with an increase in the concentration of H_3PO_4 in the initial mixture of acetone and acid; most of the mesityl oxide formed was in the fraction that distilled at about 130° (mesityl oxide boils at 129.8°). The amount of acetone that remained in the residual acid increased markedly when the original acid concentration was raised from 75 to 85% H_3PO_4 (Figure 7). When the acid in the initial acid-acetone mixture was less concentrated than 75% H_3PO_4, the amounts of both acetone and mesityl oxide in the residual acid were quite small—less than 2 cg/300 ml of initial acid. The residual acid from the distillation of acetone from its mixture with 65% H_3PO_4 developed no color from residual organics when heated to 350°. These results indicate that the distillation of the acetone fraction that is obtained in the extraction of wet-process acid may result in only small losses of acetone for recycle if the extract contains enough water to keep the concentration of H_3PO_4 no higher than 65%.

DISCUSSION OF RESULTS

The separation of impurities from wet-process phosphoric acid by each of the four solvents—1-butanol, 1-heptanol, methyl ethyl ketone, and acetone—was increased by partial ammoniation of the acid, but the ammoniation decreased the extraction of P_2O_5. With ammoniation to a mole ratio $NH_3:H_3PO_4$ of 0.1, 80% of the P_2O_5 was extracted with only 20% of the major impurities, including ammonia.

Of the four solvents tested intensively, acetone was the most effective extractant of P_2O_5, followed closely by methyl ethyl ketone and 1-butanol; 1-heptanol was least effective.

1-Butanol extracted more P_2O_5 than did 1-heptanol, but 1-heptanol required less water than 1-butanol to strip the acid from the organic layer, so that the concentration of H_3PO_4 in the purified acid was about the same for both alcohols. The overall heat requirement for evaporation of water from the extracted acids would be about the same for extraction with either alcohol.

1-Heptanol is so insoluble in water that no separate step would be required for its recovery. The dissolved 1-butanol in both the extracted acid and the raffinate would have to be recovered, probably by distillation.

Both methyl ethyl ketone and acetone would be recovered by distillation, and the loss of either solvent would be very small.

The energy requirements and the ease of operation must be considered in comparing the use of an alcohol with that of a ketone in the purification of wet-process phosphoric acid. The stripping with water, concentration of purified acid, and recovery of the solvent alcohol should be compared with the simultaneous distillation of ketone and concentration of the purified acid. Final evaluation of the two different processes should be made on the basis of results of tests on a larger than laboratory scale.

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Photochemistry of Bioactive Compounds.
# 1-(4-Chlorophenyl)-3-(2,6-dihalobenzoyl)ureas

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The photoproducts obtained upon irradiation at 300 nm of 1-(4-chlorophenyl)-3-(2,6-dichlorobenzoyl)urea (I) and 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea (II) in methanol solution and in the solid phase were identified. Photolysis of I yielded p-chlorophenyl isocyanate, N-4-chlorophenyl methylcarbamate, N-phenyl methylcarbamate, 2-chlorobenzamide, and 2,6-dichlorobenzamide. The photoproducts of II were identified as p-chlorophenyl isocyanate, N-4-chlorophenyl methylcarbamate, N-phenyl methylcarbamate, and 2,6-difluorobenzamide. Mechanistic pathways are examined and discussed. The possibility of a type II disproportionation is considered.

The photochemistry of urea-based herbicides has received considerable attention recently (Mazzochi and Rao, 1972; Crosby and Tang, 1969). The major reaction pathways observed involve either photodechlorination or carbamate formation in the presence of methanol. When water is used as solvent hydration products have been detected (Rosen *et al.,* 1969).

It was of interest to determine the photoproducts arising from systems containing more than one amide bond. 1-(4-Chlorophenyl)-3-(2,6-dichlorobenzoyl)urea (I) and 1-(4-chlorophenyl)-3-(2,6-difluorobenzoyl)urea (II) were chosen for study since both the reactivities of the halogen and amide bonds could be studied.

I, X = Cl
II, X = F
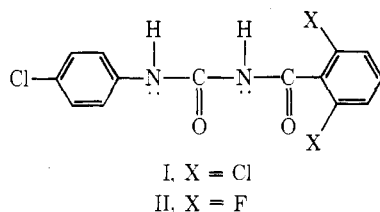
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EXPERIMENTAL SECTION

Materials. Compounds I and II were obtained from Thompson-Hayward Chemical Co. (Kansas City, Kan.) under the designations TH 6038 and TH 6040, respectively. The samples were purified by recrystallization from methanol and acetone until pure by thin-layer chromatography (tlc).

Standards. 2,6-Dichlorobenzamide, 2-chlorobenzamide, 4-chlorophenyl isocyanate, and phenyl isocyanate were obtained from Aldrich Chemical Co. and used without further purification. N-p-Chlorophenyl and N-phenyl methylcarbamates were prepared by refluxing the respective isocyanates in methanol for 6 hr. This method gave a >90% yield of the methylcarbamates.

All samples prepared or commercially obtained were authenticated by gas chromatography (gc) and/or mass spectrometry.

Solvents. The methanol used in the photoreactions was obtained from Mallinckrodt Chemical Works in Spectrophotometric Grade. The methanol, benzene, and acetone used as tlc or extraction solvents were glass distilled (Burdick and Jackson Laboratories, Muskegon, Mich.).

Photochemical Equipment. All photolyses were carried out in a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co.) fitted with RUL 3000 lamps having a peak energy output at 300 nm. During irradia-