

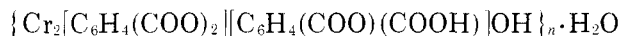
Heavy Metal Terephthalates

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Simple terephthalates of divalent iron, cobalt, nickel, copper, and manganese, and of silver and lanthanum were prepared by metathesis from sodium terephthalate and the corresponding metal ion solutions. Fe(III), Cr(III), and Ni formed insoluble basic salts. The basic ferric terephthalate gave iron oxide and free terephthalic acid on extensive hydrolysis. Fe(II) and Co(II) terephthalates split off terephthalic acid and became dimetallic basic terephthalates at 270°C in water. The water solubilities, stabilities toward acetic acid, and compositions were investigated. The infrared spectra and x-ray diffraction patterns are presented. The probable forms of iron impurities formed during the manufacture and purification of terephthalic acid are discussed.

THE manufacture of terephthalic acid (TPA) free from metals is necessary for providing color-free polymers. Little information is available in the literature concerning salts of heavy metals with TPA, especially those formed as corrosion products from stainless steel reactors. A dark brown precipitate was prepared by Weinland and Paschen (1915) from sodium terephthalate and ferric chloride, but because of its insolubility, no attempts were made to characterize it. Küntzel and Walther (1963) found that chromium formed salts with ortho- and isophthalic acids, but the terephthalates were not fully characterized. By analogy with the phthalates, they suggested for the terephthalates the formula

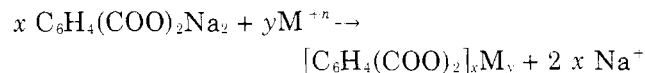


After termination of the present work, a thermal decomposition study on nickel terephthalate, $NiC_6H_4(COO)_2 \cdot 4H_2O$, was reported by Acheson and Galwey (1967).

The objective of our work was to study the properties of selected heavy metal-terephthalic acid compounds which might relate to terephthalate polymer color, hoping that the knowledge gained of the solubilities and stabilities of these compounds would suggest means for preventing

their formation or for providing means for their removal during terephthalic acid (TPA) manufacture—i.e., by oxidation of *p*-xylene followed by purification of crude TPA thus obtained using acetic acid as a solvent.

Divalent metal terephthalates such as those of Fe, Co, Ni, Cu, and Mn, and also La and Ag terephthalates, were prepared by methathesis from sodium terephthalate and the corresponding metal ion solution.



Except for Ag and La, the terephthalates were colored crystalline hydrates. On prolonged boiling in water, some of these hydrates were hydrolyzed to insoluble basic salts—e.g., $Fe(OH)C_6H_4(COO)_2$. The iron compound was simultaneously oxidized during hydrolysis in air. On prolonged treatment with water at high temperature (270°C) the iron basic salt was completely hydrolyzed to the hydrated iron oxide and free TPA.

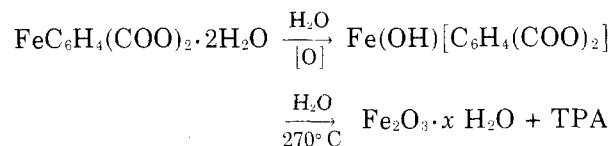
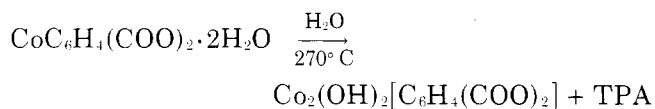
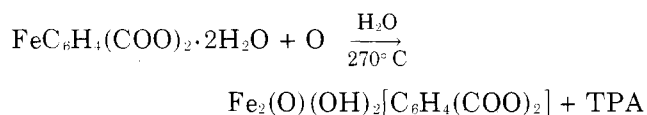


Table I. Analytical Results of Metal Terephthalates

Metal	Formula ^a	Color	Yield, %	Elemental Analysis									
				C		H		O		M		H ₂ O	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Fe	$Fe(TPA) \cdot 2H_2O$	Yellow	80	37.53	36.98	3.15	2.96	37.50	37.30	21.81	21.70
	$Fe(OH)TPA$	Brown	100	40.55	38.92	2.12	2.69	33.76	35.00	23.57	23.90
	$Fe_2(O)(OH)_2TPA$	Red brown	90	29.56	32.10	1.86	2.25	34.37	33.40	34.28	34.65
Co	$Co(TPA) \cdot 2H_2O$	Pink	93	37.09	36.52	3.11	3.27	37.05	36.70	22.75	20.60	13.91	11.90
	$Co_2(OH)_2TPA$	Lt. brown	95	30.41	30.82	1.91	2.19	30.38	29.80	37.30	36.24
Ni	$Ni(TPA) \cdot 4H_2O$	Green	98	32.58	34.73	4.10	3.72	43.41	40.41	19.91	19.40	24.44	24.01
	$Ni(OH)(TPAH)H_2O$	Green	98	37.12	37.00	3.12	3.23	37.09	37.70	22.68	22.15	6.95	5.27
Cr	$Cr(OH)TPA$	Gray	90	41.22	41.44	2.16	3.12	34.32	35.40	22.30	18.20
Mn	$Mn(TPA) \cdot 2H_2O$	Rose	87	37.67	37.96	3.16	3.24	37.63	36.20	21.54	21.15	14.13	14.60
		White											
Cu	$Cu(TPA) \cdot 3H_2O$	Blue	96	34.11	33.98	3.58	3.68	39.76	37.7	22.56	22.75	19.23	18.21
Ag	Ag_2TPA	White	96	25.29	25.09	1.06	1.15	16.85	17.50	56.79	57.10
La	$La_2(TPA)_3 \cdot 4H_2O$	White	95	34.23	34.25	2.39	2.69	30.42	29.80	32.99	33.73	8.56	7.84

^aTPA, $C_6H_4(COO)_2$.

The ferrous and cobaltous terephthalate dihydrates gave different types of hydrolysis products when treated in an autoclave at 270°C with water and air under 70-atm pressure. Each molecule split off one mole of TPA, and binuclear basic salts were formed.



Analytical results are given in Table I.

Some of the salts, such as those of Fe, Co, and Ni, are slightly soluble in water. All simple hydrates decompose readily in boiling glacial acetic acid, giving the metal acetate in solution and precipitating free TPA. All basic salts are insoluble in water. They vary in their stability toward glacial acetic acid and dilute solutions such as

5% aqueous acetic acid. The basic chromium salt resists the attack of boiling 5% acetic acid, whereas the basic iron salt partially decomposes; prolonged reflux (3 to 4 hours) in this solvent causes complete decomposition into soluble ferric acetate and free TPA. The oxodiferric and dicobalt basic terephthalates decompose readily in boiling dilute or glacial acetic acid.

The infrared spectra of the compounds are shown in Figure 1. The simple hydrates showed the characteristic hydroxyl-stretching band of the free water molecule at 3200 to 3300 cm^{-1} . The nickel hydrate, $\text{Ni}(\text{C}_6\text{H}_4\text{COO}) \cdot 4\text{H}_2\text{O}$, additionally showed rocking and wagging vibration modes for 970 and 825 cm^{-1} , respectively. These bands are intense, probably activated by strong coordination of the water molecules in the sphere of the metal, and absorb very strongly in the spectra. All basic salts showed a broad finger-shape association band between 1100 and 1200 cm^{-1} , which is assigned to the bending mode of the M-O-H vibration in the hydroxy-bridged complexes, as suggested by Nakamoto (1963). This band is particularly well defined in the basic ferric terephthalate.

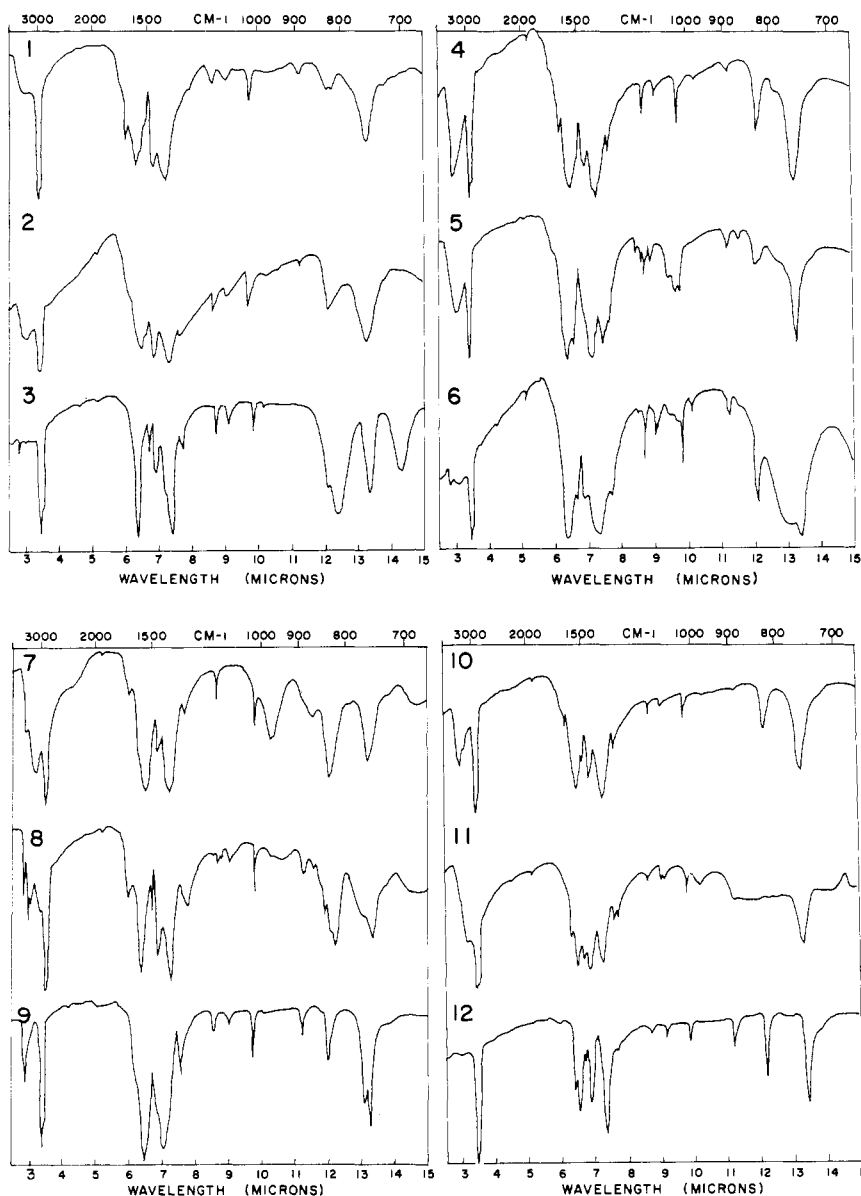


Figure 1. Infrared spectra of metal terephthalates

1. Basic chromium terephthalate
2. Cobalt terephthalate
3. Dicobalt basic terephthalate
4. Ferrous terephthalate
5. Basic ferric terephthalate
6. Diferric oxobasic terephthalate
7. Nickel terephthalate
8. Basic nickel terephthalate
9. Lanthanum terephthalate
10. Manganese terephthalate
11. Copper terephthalate
12. Silver terephthalate

Table II. X-Ray Powder Diffraction Patterns

d Spacing, A	I/I_1	d Spacing, A	I/I_1	d Spacing, A	I/I_1	d Spacing, A	I/I_1	d Spacing, A	I/I_1	d Spacing, A	I/I_1	d Spacing, A	I/I_1		
Fe(TPA) ^c ·2H ₂ O ^b				Fe(OH)TPA ^b				Fe(O)(OH) ₂ TPA ^b				Co(TPA)·2H ₂ O ^b			
9.18	100	9.68	100	10.0	100	9.89	9								
7.02	8	6.95	14	6.43	10	8.97	100			2.948	12	2.880	8		
6.17	84	6.13	28	5.59	16	6.12	72			2.862	11	2.830	15		
4.82	40	5.69	9	4.98	26	4.78	40			2.798	10	2.805	9		
4.58	28	5.45	44	3.33	8	4.54	23			2.660	10	2.685	7		
4.01	10	4.91	11	3.09	9	4.50	19			2.640	13	2.550	10		
3.62	17	4.83	24	3.01	9	3.78	15			2.408	7	2.315	9		
3.56	13	4.65	11	2.96	9	3.60	19			2.294	11	2.245	17		
3.076	39	4.54	8	2.94	11	3.26	7			2.255	7	2.198	9		
2.976	40	4.16	7	2.761	31	3.043	38			2.151	7	2.165	9		
2.653	20	3.456	12			2.958	35			2.121	7	2.010	10		
2.570	9	3.368	15			2.761	9			1.994	16				
2.440	7	3.326	15			2.645	19			1.903	8				
2.170	15	3.112	9			2.627	10								
2.058	10	3.059	12			2.234	7								
1.943	7	3.024	9			2.154	11								
1.874	7	2.991	9			2.062	7								
		2.830	20			2.048	11								
		2.789	21												
		2.627	7												
		2.165	11												
		2.104	8												
		1.721	7												
Co(OH) ₂ TPA ^b				Ni(TPA)·4H ₂ O ^c				Ni(OH) ₂ TPA·2H ⁺ ^c				Cr(OH)TPA			
9.89	100	10.45	100	9.50	100	14.4	100								
5.54	9	6.52	79	7.49	28	10.25	50								
4.95	26	5.73	29	7.21	20	5.05	10								
3.06	7	5.08	45	5.68	58										
2.942	7	4.50	48	4.84	24										
2.896	15	3.87	8	4.76	22										
2.708	22	3.81	29	3.75	41										
2.399	8	3.40	58	3.065	26										
1.983	8	3.24	10	2.940	8										
Mn(TPA)·2H ₂ O ^c				Cu(TPA)·3H ₂ O ^c				Ag ₂ (TPA) ^c				La ₂ (TPA) ₃ ·4H ₂ O ^c			
9.35	100	11.45	100	6.72	100	9.80	100								
6.15	21	6.58	11	5.36	48	8.00	8								
4.82	7	5.37	27	4.91	19	6.22	42								
4.60	13	5.11	13	4.72	54	5.78	27								
3.10	7	4.55	8	3.55	24	5.01	35								
3.00	7	3.82	14	3.48	25	4.93	34								
2.67	8	3.42	7	3.15	34	4.89	38								
		2.86	8	2.98	9	4.75	15								
		2.294	7	2.888	94	4.31	9								
		1.996	10	2.780	40	5.10	16								
				2.658	24	3.99	19								
				2.625	28	3.80	15								
				2.221	33	3.69	22								
				2.120	24	3.52	7								
				1.903	9	3.16	21								
				1.870	9	3.06	20								
				1.740	7	2.98	25								
				1.575	11	2.92	11								
						2.635	8								
						2.590	11								
						2.48	7								
						2.42	7								

^aTPA, C₆H₄(COO)₂²⁻. ^bCo K α , Fe filter. ^cCu K α , Ni filter. d spacings obtained from strip-chart recordings; intensities obtained from peak heights.

The spectra of the dimetallic basic terephthalates of Co and Fe, Co₂(OH)₂[C₆H₄(COO)₂]₂ and Fe₂(O)(OH)₂[C₆H₄(COO)₂]₂, have interestingly similar features. Neither compound shows the broad band of water between 3200 and 3400 cm⁻¹. Each has a sharp OH-stretching vibration band at 3590 cm⁻¹ similar to that of the hydroxides of metals. The basic nickel terephthalate also exhibits this band. In these three compounds, the asymmetric stretching vibrations of the carboxylate group are found at 1590 cm⁻¹; the same vibrations in ferrous, cobalt, nickel, copper, manganese, and lanthanum terephthalates are at 1550 cm⁻¹. These differences might indicate that the carboxylate group is a bit more strongly coordinated in the former three compounds than in the latter six. These assignments are consistent with the corresponding assignments made by Nakamoto *et al.* (1961) and Nakamoto (1963) and agree well with the ionic carboxylate vibration of sodium terephthalate at 1550 cm⁻¹. Both the ionic and coordinated carboxylate bands were found at somewhat lower frequencies than the carboxylate band of terephthalic acid, 1690 cm⁻¹. The shift in the band position of this group toward higher frequency for ionic terephthalate < coordinated < covalent (terephthalic acid) is thus demonstrated.

Analysis, by the Fischer reagent method, for water for NiC₆H₄(COO)₂·4H₂O was 26.70% (calculated 26.68%), in good agreement with the results reported by Acheson and Galwey (1967), measured by absorption on magnesium perchlorate. However, it is most likely that their salt C, prepared by prolonged boiling of nickel carbonate and TPA in water, is the basic nickel terephthalate, Ni(OH)C₆H₄(COO)(COOH)·H₂O, which was prepared in this laboratory by digesting the tetrahydrate in boiling water. Their microanalytical results are close to ours for this composition.

Analyses of the Cu, La, and basic Ni terephthalates for water by the Fischer reagent method gave values consistently lower than the calculated values—for example, Cu(TPA)·3H₂O gave analyses of 15.1 to 16.6%, suggesting 2.5 H₂O, and La₂(TPA)₃·4H₂O results varied between 1.9 and 2.3% or 1 H₂O. However, heating samples of these compounds under 1 mm of Hg vacuum in a drying tube over refluxing trimethylene glycol for 6 hours gave values approaching theory. It seems that part of the water in these compounds is tightly bound to the anion. This agrees with the discussion of Moeller (1952) on the occurrence of water in inorganic compounds.

The x-ray diffraction patterns (Table III) were useful

for identification and classification. The patterns of the dihydrates of divalent iron, cobalt, and manganese terephthalates showed certain similarities in the angle positions of the main lines, which indicate that these salts might have similar molecular structure, although not necessarily the same lattice parameters. Also, a striking similarity between the dicobalt and diferric basic salts was apparent.

Discussion

One of the well known processes for the manufacture of TPA is composed of air oxidation of *p*-xylene in acetic acid in presence of cobalt catalyst; separation of the crude TPA from the reaction medium, followed by washing; recrystallization from water or aqueous acetic acid; and/or final purification to reduce aldehydic impurities.

During the air oxidation of *p*-xylene in acetic acid, iron is believed to be leached out of the stainless steel reactors as ferrous iron by acetic acid and TPA at the temperature of the reaction, 130° to 150°C. It is then air-oxidized immediately to the ferric state, most likely to an acetic acid-soluble form. If TPA is then separated from the reaction medium and washed thoroughly or digested with acetic acid in nonferrous containers, most of the iron should be removed. However, if washing is incomplete and if water or a water-acetic acid mixture is used for washing at high temperature, the soluble iron incorporated in the TPA particles hydrolyzes to the less soluble basic iron acetate and terephthalate. If TPA is then recrystallized from water (at 160° to 270°C), the iron hydrolyzes further to the hydrated ferric oxide. This step was demonstrated by treating suspensions of either basic iron acetate or terephthalate in water at 270°C for 15 minutes. In both cases, iron oxide was formed quantitatively. Once iron oxide is formed, it is difficult to remove, even by retreatment with acetic acid.

During TPA purification by reduction of aldehydic impurities in aqueous medium in stainless steel containers, iron might be introduced as corrosion products. It might also have been left in the TPA cake by insufficient acetic acid wash. In either case, any iron in the system would be reduced to the ferrous state. Since ferrous terephthalate (and acetate) are soluble in water, they can be removed by filtration and water-washing of the TPA in the absence of air. If high temperature prevails in the aqueous medium during purification, the insoluble oxidiferric basic terephthalate forms. This, however, would be decomposed by an acetic acid afterwash. If the crude TPA contains iron oxide, reduction might not remove it. Corrosion impurities such as Ni and traces of the catalyst Co are easily removed from the crude TPA by acetic acid or water-acetic acid mixtures because of their relatively high solubilities.

To obtain polymer grade TPA free from metal ions, especially the readily hydrolyzable iron, water has to be avoided in the early stages of the process. Acetic acid is an ideal reagent in those stages.

Experimental

Materials, Apparatus, and Analysis. Reagent-grade ferrous sulfate·7H₂O, chromium nitrate·H₂O, nickel nitrate·6H₂O, copper sulfate·5H₂O, manganese sulfate·0.5H₂O, silver nitrate, and lanthanum chloride·7H₂O were used. Polymer-grade terephthalic acid was purchased from the Amoco Chemical Co.

Infrared spectra were recorded on Perkin Elmer 337 and 137 spectrophotometers, using Nujol mulls (Figure

1). X-ray diffraction patterns were recorded by a Norelco diffraction unit, using Ni-filtered Cu and Fe-filtered Cr K α radiations. Solubilities of the sparingly soluble salts were determined by spectrophotometry. Solubilities of the more soluble salts were determined gravimetrically. The solubility of ferrous terephthalate was determined by titrating the ferrous ion in the saturated solution with potassium permanganate under nitrogen.

Preparation of Ferrous Terephthalate. A disodium terephthalate solution was prepared by titrating a suspension of 16.6 grams (0.1 mole) of TPA in 300 ml of water with sodium hydroxide to a phenolphthalein end point. A solution containing 27.8 grams (0.1 mole) of ferrous sulfate, FeSO₄·7H₂O, was added to the disodium terephthalate solution at room temperature under a stream of nitrogen. A canary-yellow, crystalline precipitate which resulted was filtered and washed under nitrogen with cold water until sulfate-free, then dried at room temperature under vacuum over phosphorus pentoxide. The salt did not melt below 320°C. When heated gradually, it lost some water of crystallization at 155°C.

Ferrous terephthalate was soluble to the extent of 0.22 gram per 100 grams in water at 25°C, giving colorless solutions found to contain 1 mole of TPA per mole of Fe(II). When the clear aqueous solution was boiled in air, the ferrous ion was oxidized to the ferric state and a red product precipitated. The rate of oxidation at 100°C was measured by titrating portions of the solution for the remaining Fe(II). In the first hour, 37% of the iron was oxidized. Although the oxidation rate decreased gradually, prolonged boiling in water gave TPA and iron oxide quantitatively.

Ferrous terephthalate did not dissolve in organic solvents such as acetone and acetonitrile. In glacial acetic acid it dissolved readily at room temperature but then decomposed quickly to TPA and ferric acetate. In boiling 5% aqueous acetic acid, decomposition was slower.

Preparation of Basic Ferric Terephthalate. A suspension of 20 grams of ferrous terephthalate in 300 ml of water was boiled gently for 8 hours while a stream of oxygen gas was passed through the mixture. The yellow color of the solid changed to light brown. It was filtered and dried at 120°C for 48 hours. It did not melt below 320°C. The product was insoluble in water and in organic solvents. It decomposed to TPA and ferric acetate in refluxing glacial acetic acid and was partly decomposed in refluxing 5% acetic over long periods of time (1 hour). When a suspension of 4 grams of the product in 40 ml of water was heated in a sealed glass tube at 270°C for 2 hours, a mixture of TPA and iron oxide was obtained. The TPA was extracted with dimethyl sulfoxide (DMSO), and the insoluble brown iron oxide was identified by infrared spectrophotometry; decomposition was quantitative. Potentiometric titration of a suspension of the basic ferric terephthalate in water against standard sodium hydroxide gave a curve with a break at 1Fe:2NaOH; the third bond of Fe must already have been occupied by an OH group.

Reactions of Ferrous Terephthalate at High Temperature. Ferrous terephthalate (10 grams) was mixed with 40 ml of water and heated in a sealed glass tube at 270°C for 1 hour. A red-brown compound (9.2 grams) was obtained, together with free TPA. The mixture was separated by extracting the TPA with DMSO. The TPA was reprecipitated from DMSO by addition of excess

water. The weight balance indicated that for every 2 moles of ferrous terephthalate 1 mole of TPA and 1 mole of a new iron terephthalate were formed. The product, oxidiferrous basic terephthalate, did not melt below 320°C, was insoluble in water and in organic solvents, and did not contain any ferrous ion. Although the product was very stable on prolonged treatment in water even at high temperature (250°C) it decomposed to free TPA and a brown solution of ferric acetate in refluxing acetic acid, glacial or dilute (5%).

A sample was titrated potentiometrically with sodium hydroxide. The break in the titration curve indicated that each iron atom was bonded to one carboxylic group; the remaining two valences of iron must have been occupied by other groups such as OH^- and $\frac{1}{2}\text{O}^{2-}$. This was confirmed by infrared spectrophotometry.

Preparation of Nickel Terephthalate. A solution containing 82.3 grams of nickel nitrate heptahydrate (0.3 mole) was mixed with a 0.3M disodium terephthalate solution and stirred for 1 hour at room temperature. In a few minutes, a green crystalline product separated out. It was filtered, washed with water, and dried at 115°C for 1 hour.

Potentiometric titration of the product with standard sodium hydroxide gave a curve with one break equivalent to a dibasic nickel ion. When the product was heated for 24 hours at 120°C, it lost two waters of crystallization; it did not melt below 320°C. The solubility in water at 25°C was 0.38 gram per 100 grams. It was very soluble in ammonium hydroxide, forming a deep violet solution. It decomposed in refluxing glacial or 5% acetic acid to form nickel acetate and free TPA.

Preparation of Basic Nickel Terephthalate. Crystalline nickel terephthalate (30 grams) was refluxed in 1 liter of water for 12 hours. The colloidal, light-green precipitate that formed was filtered, water-washed, and dried. It did not melt below 320°C. Potentiometric titration of the product with standard sodium hydroxide gave a curve with a sharp break corresponding to a monosubstituted nickel atom. This indicated that at least one hydroxyl group was attached to the nickel. The same product was prepared by heating nickel terephthalate with water in a weight ratio of 1 to 10 at 270°C in sealed tubes. This also indicated that the basic salt, once formed, was stable at high temperature. The product decomposed in boiling glacial or 5% acetic acid, giving free TPA and a green nickel acetate solution.

Preparation of Basic Chromic Terephthalate. A solution containing 115 grams (0.285 mole) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was mixed with a neutral solution of disodium terephthalate (0.428 mole) and stirred for 2 hours at room temperature. The gray precipitate, which appeared after a few minutes, changed to a violet solid. It was filtered, washed with acetone, and dried. It did not melt when heated to 320°C. It was insoluble in boiling water but decomposed in refluxing glacial acetic acid. When heated in 5% acetic acid, it was stable at reflux temperature for 1 hour, but when heated at 250°C for 1 hour, it decomposed about 10%, based on liberated TPA. When heated in water, all the solid was recovered without change in composition or liberation of TPA.

Preparation of Cobalt Terephthalate. A solution containing 49.82 grams of $\text{Co}(\text{acetate})_2 \cdot 4\text{H}_2\text{O}$ (0.2 mole) in 200 ml of water was mixed at room temperature with a saturated solution of sodium terephthalate. The pink

crystalline precipitate was filtered, washed with water, and dried at 80°C. The solid did not melt below 240°C, but turned dark blue at this temperature. It decomposed in glacial acetic acid to cobalt acetate and TPA. The solubility of cobalt terephthalate in water, 0.28 gram per 100 grams at 25°C, decreased with increasing temperature because of the formation of the less soluble basic salt. When the crystalline salt was titrated potentiometrically with standard HCl, the break in the curve occurred at a ratio of 1 Co to 1 TPA. Analysis gave 22.8% Co, compared with 22.75% calculated for the dihydrate.

Preparation of Dicobalt Terephthalate Basic. Cobalt terephthalate dihydrate (150 grams, 0.58 mole) was heated with 1.5 liters of water for 1 hour in an autoclave at 270°C and 70-atm pressure. The reaction mixture was cooled to room temperature, discharged, filtered, water-washed, and dried at 90°C. The infrared spectra indicated that the solid was a mixture of TPA and a new compound. The solid was slurried with 30 ml of DMSO for 1 hour, filtered, washed in turn with dimethyl formamide, acetone, and ether, and dried. When excess water was added to the filtrate, TPA (0.29 mole) was precipitated. The light-brown cobalt product was free of TPA, as shown by its spectrum. It was insoluble in water and could not be titrated potentiometrically. It did not melt below 300°C and did not change color to deep blue as did the dihydrate. It decomposed slowly in boiling glacial acetic acid, giving cobalt acetate and TPA.

Preparation of Cu, Ag, Mn, and La Terephthalates. The general procedure for the preparation of these salts was essentially similar to that for the preparation of Fe(II), Ni, and Co hydrates. Stoichiometric quantities of sodium terephthalate and of $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, AgNO_3 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ were mixed in aqueous solutions, and the solids formed were separated and dried at 90°C overnight. They all decomposed in boiling glacial acetic acid, giving the soluble metal ion acetate and free TPA. Copper terephthalate did not melt below 300°C. It lost water of crystallization at 230° to 240°C, changing from blue to green. Potentiometric titration with standard HCl gave a curve with a break corresponding to one Cu atom:one carboxylic ion. The silver salt was more stable to direct sunlight than was AgNO_3 . Both Cu and Ag terephthalates dissolved readily in ammonium hydroxide. The Mn salt dissolved in ammonium hydroxide, but the solution deposited gelatinous hydroxide on standing. Solubilities in water at 25°C were: 0.0022 gram $\text{Cu}(\text{TPA}) \cdot 3\text{H}_2\text{O}$ /100 grams, 0.0025 gram $\text{Ag}_2(\text{TPA})/100$ grams, 0.020 gram $\text{Mn}(\text{TPA}) \cdot 2\text{H}_2\text{O}/100$ grams, and 0.0066 gram $\text{La}_2(\text{TPA})_3 \cdot 4\text{H}_2\text{O}/100$ grams.

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