

that at ordinary temperatures the solubility of ammonium nitrate exceeds that of any of the other materials listed. Its solubility is also influenced by temperature to a greater degree than that of any other fertilizer material. Temperature changes, on the other hand, have relatively little effect on the solubility of some materials, as ammonium sulfate. The high solubility of ammonium nitrate and the marked effect of temperature on its solubility are important factors influencing its tendency to cake, as discussed later in greater detail.

DETERMINATION OF MOISTURE CONTENT

A slight change in the moisture content of soluble fertilizer salts has been shown to have a greater effect on their mechanical condition than a corresponding small change in any other factor that affects their tendency to cake (3). It was felt that this should hold particularly true for ammonium nitrate, because of its high solubility and wide variation in solubility with temperature. An accurate method for the determination of moisture in ammonium nitrate became imperative therefore if any progress was to be made in improving its mechanical condition.

It is known that ammonium nitrate undergoes slow decomposition at 100° C., and it did not seem, therefore, that the official method (4) was adapted to the determination of moisture in a material of this kind. With a view to finding a suitable method, sets of standard ammonium nitrate samples were prepared and submitted to a number of laboratories in which determinations for moisture in this material are known to have been made. The samples were accompanied by the request that they be analyzed by such methods as are considered best suited for the determination of their moisture content. The standard samples prepared for this collaborative study are given in table 6 and the results in table 7.

Standard sample ANPL No. 1 was selected from a commercial shipment that had been stored in a dry place. Sample ANPL No. 2 was also selected from a commercial shipment, but its moisture content was increased by spraying with water while it was being rolled in a rotating drum. Sample WCW No. 3 was collected at the plant before it was dried to the point desired for shipment. TVA samples Nos. 4 and 5 were taken from commercial shipments that had been stored in bags for a period of 3 months at 55° F. at a relative humidity of 80

TABLE 6.—Standard ammonium nitrate samples¹

Source and sample No.	Type of granules	Treatment	Moisture in sample
Alberta Nitrogen Products, Ltd.:			
ANPL No. 1.....	Sprayed.....	None.....	Original.
ANPL No. 2.....	do.....	0.5 percent WP + 3.5 percent Kittitas.	Added.
Welland Chemical Works, Ltd.:			
WCW No. 3.....	do.....	None.....	Original.
Tennessee Valley Authority:			
TVA No. 4.....	Grained.....	do.....	Absorbed.
TVA No. 5.....	do.....	1.0 percent PRP + 4.0 percent Cellite.	Do.
Military Chemical Works, Inc.:			
MCW No. 6.....	Monocrystalline.....	None.....	Original.
MCW No. 7.....	do.....	do.....	Do.

¹ Results of analyses shown in table 7.

TABLE 7.—Moisture in standard ammonium nitrate samples

Collaborator	Method	Moisture in samples ¹ —						
		ANPL No. 1	ANPL No. 2	WCW No. 3	TVA No. 4	TVA No. 5	MCW No. 6	MCW No. 7
		<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>
Alberta Nitrogen Products, Ltd.	2 hours in oven at 90° C.	0.13	2.97	0.74	0.75	0.92	0.17	0.75
Do.....	Fisher (14)	.09	2.52	.72	.70	.99	.09	.85
Hercules Powder Co....	2 hours in oven at 95° C.	.11	2.70	.50	.57	.85	.11	.44
Solvay Process Co.....	2 hours in vacuum at 80° C.	.09	2.67	.80	.68	.83	.07	.71
Division of Soils, Fertilizers, and Irrigation.	20 hours in oven at 70° C.	.08	2.91	.74	.75	.78	.08	.66
Do.....	Air at 70° C. through sample for 4 hours.	.07	2.89	.80	.79	.80	.08	.60
Consolidated Mining & Smelting Co., Ltd.	4 hours in oven at 80° to 85° C.	.08	2.75	.72	.65	.80	.08	.55
Welland Chemical Works, Ltd.	Dry air at 65° to 70° C. through sample for 40 minutes.	.07	2.69	.78	.61	.70	.06	.33
Military Chemical Works, Inc.	5 hours in oven at 70° C.	.06	2.59	.64	.47	.71	.11	.47
Do.....	2 hours in oven at 100° C.	.08	2.76	.71	.56	.88	.09	.42
Eastern States Farmers' Exchange.	Air at 60° C. through sample for 3 hours.	.09	2.73	.78	.58	.77	.09	.47
Do.....	5 hours in oven at 100° C.	.11	2.79	.76	.61	.81	.09	.43
Tennessee Valley Authority.	Dry air at 60° C. through sample for 6 hours.	.07	2.72	.75	.78	.81	.08	.67
Do.....	Dry air at 70° C. through sample for 5 hours.	.08	2.68	.91	.83	.79	.10	.60
Do.....	20 hours in oven at 70° C.	.09	2.84	.82	.71	.83	.09	.73
Mean.....		.09	2.75	.75	.67	.82	.09	.58

¹ See table 6 for type of granules and treatment.

percent. Samples MCW Nos. 6 and 7 were prepared on a pilot-plant scale; No. 6 was dried as completely as was considered practical under commercial conditions, and No. 7 was represented as being only partially dried. The moisture in samples ANPL No. 1, WCW No. 3, and MCW Nos. 6 and 7 represents original moisture that had not been eliminated by drying, while that in samples ANPL No. 2 and TVA Nos. 4 and 5 represents moisture that had been added or absorbed subsequent to drying.

The results reported by the collaborators for the moisture in the samples and the methods used in the determination of moisture as shown in table 7 show good agreement in general, considering the hygroscopic nature of the samples submitted for analysis. The results obtained with the Fisher method (14) show good agreement with the average values, but this method is not considered to be adapted to general use in fertilizer laboratories for the reason that it gives water of hydration in addition to free moisture in materials and mixtures containing water of hydration. The other methods used by the collaborators may be considered as adaptations of the following three methods: (1) Drying in an air oven at 70° C. for 20 hours; (2) drawing air at 70° C. through the sample for 2 hours; or (3) drying in a vacuum at room temperature over Anhydron for 20 hours.

Moisture was determined by these three methods in samples ANPL No. 2, WCW No. 3, TVA No. 4, and MCW No. 7. The results obtained are given in table 8, which shows that the first two procedures

TABLE 8.—*Rates at which standard samples of ammonium nitrate decrease in weight on drying by different methods*

AIR OVEN AT 70° C.

Time of drying (hours)	Loss in weight of sample			
	ANPL No. 2	WCW No. 3	TVA No. 4	MCW No. 7
	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>	<i>Percent</i>
6.....	2.83	0.66	0.66	0.48
12.....	2.88	.72	.73	.59
18.....	2.90	.74	.75	.65
24.....	2.88	.74	.75	.67
30.....	2.92	.76	.78	.68

AIR FLOW AT 70° C.

1.....	2.82	0.58	0.73	0.41
2.....	2.87	.72	.77	.57
3.....	2.90	.82	.81	.71
4.....	2.90	.85	.81	.75
5.....	2.93	.89	.83	.78

VACUUM OVER ANHYDRONE AT ROOM TEMPERATURE

6.....	2.79	0.36	0.65	0.28
12.....	2.80	.36	.69	.28
18.....	2.82	.38	.70	.28
24.....	2.85	.40	.73	.29
30.....	2.85	.39	.73	.29

give closely agreeing results for moisture in all samples tested and that the method of drawing air at 70° C. through the sample for 3 hours is equivalent to 24-hours' drying in an air oven at the same temperature. The air-flow method has the advantage, therefore, of being more rapid than drying in an air oven and for this reason it is better adapted for use in control work.

The table further indicates that samples ANPL No. 2 and TVA No. 4, which contain only added or absorbed moisture, can be completely dried in a vacuum over Anhydronc in 24 hours, but that this method of drying does not eliminate within the same period all the original moisture in such samples as WCW No. 3 and MCW No. 7. The results indicate that a part of the original moisture in ammonium nitrate is present as occluded moisture and that this moisture is more difficult to remove than absorbed moisture.

The moisture in monocrystalline ammonium nitrate, which drying in vacuum over Anhydronc failed to remove, amounts to about 0.35 percent of the weight of the crystal. The data in table 2 indicate that nearly 2 percent of the volume of MCW crystals is void. It must follow, therefore, that the greater part of the void space in the crystals is filled with air rather than water.

HYGROSCOPICITY

A material is said to be hygroscopic when it absorbs moisture from the air at ordinary temperatures and humidity. This occurs when the pressure of water vapor in the air exceeds that of the saturated

solution of the material. The relative hygroscopicity of the more common fertilizer materials as determined by Adams and Merz (2) is indicated in table 9, which shows that calcium nitrate is the most

TABLE 9.—*Relative hygroscopicities of soluble fertilizer materials*

Fertilizer material	Humidity of air in equilibrium with saturated solution of material at—						
	10° C.	15° C.	20° C.	25° C.	30° C.	40° C.	50° C.
	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Calcium nitrate	—	55.9	55.4	50.5	46.7	35.5	—
Ammonium nitrate	75.3	69.8	66.9	62.7	59.4	52.5	48.4
Sodium chloride	76.6	77.0	77.6	75.5	75.2	74.7	74.1
Sodium nitrate	78.0	76.8	77.1	74.4	72.4	70.1	67.3
Ammonium chloride	79.5	79.2	79.3	76.0	77.2	73.7	71.3
Ammonium sulfate	79.8	79.3	81.0	81.8	79.2	78.2	77.8
Urea	81.8	79.9	80.0	75.8	72.5	68.0	62.5
Potassium chloride	88.3	86.2	85.7	83.4	84.0	81.2	80.0
Potassium nitrate	97.0	95.6	92.3	92.0	90.5	87.9	85.0
Monoammonium phosphate	97.8	97.0	91.7	91.9	91.6	90.3	88.2
Monocalcium phosphate	97.9	98.8	94.1	96.0	93.7	94.5	94.6
Monopotassium phosphate	98.0	98.4	96.2	95.4	92.9	92.9	92.6
Potassium sulfate	99.1	99.7	98.5	98.8	96.3	95.7	95.8

hygroscopic, ammonium nitrate is next, and potassium sulfate is the least hygroscopic of the soluble fertilizer materials.

TEMPERATURE AND HUMIDITY RELATIONS

The temperature and humidity relationships that influence moisture absorption by ammonium nitrate can best be understood by reference to figure 4. The curves in the figure show (1) the variations in the pressure of saturated aqueous vapor in the air (absolute humidity, or 100 percent relative humidity) at different temperatures between 0° C. (32° F.) and 50° C. (122° F.); (2) the aqueous vapor pressures for the same temperature range at 60, 65, 70, and 75 percent saturation (relative humidities); and (3) the vapor pressures of saturated solutions of ammonium nitrate at different temperatures between 0° and 50° C. (2). The ammonium nitrate curve cuts the curves corresponding to relative humidities of 75, 70, 65, and 60 percent at temperatures of 10°, 15°, 21.5°, and 28.5° C., respectively.

This means that at these temperatures ammonium nitrate is in equilibrium with the water vapor in the air at the relative humidities indicated, or, in other words, that the pressure of the water vapor in the air at each specified temperature and humidity is equal to that of a saturated solution of ammonium nitrate at the same temperature. If the water vapor in the air at any given temperature exceeds that of a saturated solution of ammonium nitrate at the same temperature, moisture will be absorbed. If the conditions are reversed, however, so that the water vapor in the air is less than that of a saturated solution of ammonium nitrate, a drying of the material will take place as a result of loss of moisture to the surrounding air.

The curves in figure 4 further show that at temperatures below freezing, the pressure of saturated or partially saturated water vapor in the air is very small compared with that in the air at summer temperatures. It would be expected, therefore, that ammonium nitrate would exhibit little tendency to absorb moisture from the air at temperatures below freezing, even when the relative humidity approaches 100 percent.

A saturated solution of ammonium nitrate has a vapor pressure of 18.9 mm. of mercury at 30° C. (86° F.). The aqueous vapor pressure of the air at the same temperature and a relative humidity, for example, of 50 percent is only 15.8 mm. Ammonium nitrate will therefore not absorb any moisture from the air under these conditions. If the temperature were to drop to 20° C. (68° F.) without change in the water vapor in the air, the aqueous vapor pressure would then remain the same at 15.8 mm., but the relative humidity would have increased to 90 percent. If the ammonium nitrate were not allowed

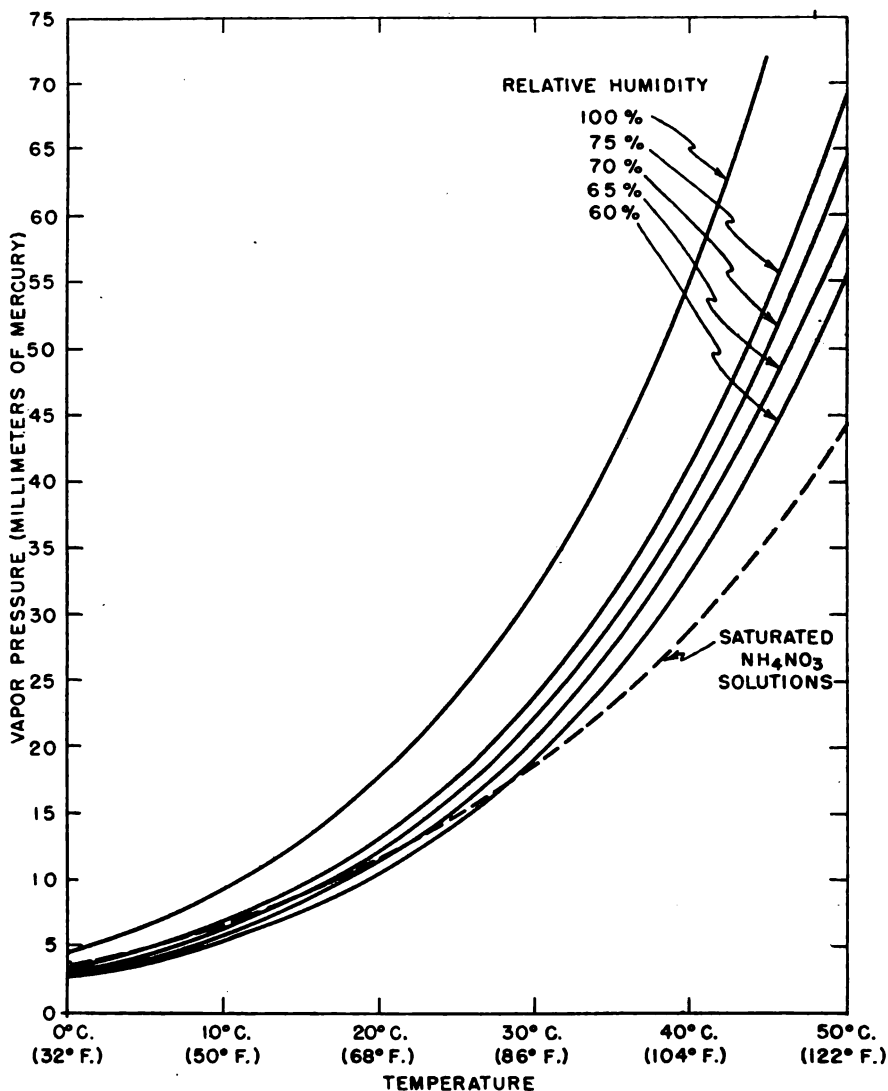


FIGURE 4.—Variations with temperature of (1) the aqueous vapor pressure in air corresponding to various relative humidities; and (2) the vapor pressure of saturated ammonium nitrate solutions.

to cool during the same interval, the vapor pressure of its saturated solution would still remain at 18.9 mm. and no absorption of moisture would take place, as the relative humidity of the surrounding air is increased to 90 percent. If the temperature of the ammonium nitrate is allowed to decrease with decrease in the temperature of the air, however, the vapor pressure of its saturated solution at the lower temperature of 20° C. will be only 11.7 mm. as compared with an aqueous vapor pressure of 15.8 mm. in the surrounding air, and a marked absorption of moisture will then take place.

If ammonium nitrate were to be granulated by the spraying method in a very humid section of the country, it might be expected that the air in the spraying tower would have to be dried if absorption of moisture by the sprayed material is to be prevented. That this is not necessary is shown in figure 4. According to the figure the vapor pressure of a saturated solution of ammonium nitrate at 45° C. (113° F.) is 35 mm. This is higher than that represented by the pressure (32 mm.) of water vapor in the air at 30° C. and a relative humidity of 100 percent. It follows therefore that if sprayed ammonium nitrate is not cooled below a temperature of 45° C. in the spraying tower it will not absorb any moisture at air temperatures below 30° C., even at a relative humidity of 100 percent. It should not be necessary therefore to dry the air passed through the tower in the process of spraying ammonium nitrate, provided the nitrate is collected at a temperature 10° to 15° C. above that of the surrounding air.

These observations show that ammonium nitrate can be stored without danger of moisture absorption (1) by maintaining the relative humidity of the air below that at which ammonium nitrate absorbs moisture, or (2) by maintaining the ammonium nitrate at a temperature about 10° C. above that of the surrounding air.

The relative humidity of the air below which ammonium nitrate does not absorb moisture varies from 75 percent at 10° C. (50° F.) to 52 percent at 40° C. (104° F.). The pressure of water vapor in the air at 10° C. and a relative humidity of 75 percent amounts to about 7 mm. At 40° C. and the same relative humidity the pressure of water vapor in the air is about 41.5 mm., or nearly six times as great. This explains why ammonium nitrate absorbs moisture more rapidly during hot weather than in winter and why the relative humidity alone gives little or no indication of the behavior of ammonium nitrate with respect to moisture absorption. To know this the temperature also must be specified. Inasmuch as the temperature varies greatly in different sections of the country and in the same section at different seasons, the behavior of ammonium nitrate in different localities and at different seasons may vary greatly, even if the relative humidity were to remain unchanged.

LOCATION AND HUMIDITY RELATIONS

Data on the manner in which ammonium nitrate is likely to behave under normal conditions in different parts of the country are given in table 10. This table shows for each month (1) the average monthly temperature over a period of 20 years for the places listed (13); (2) the average monthly aqueous vapor pressure over the same period; and (3) the difference between the average aqueous vapor pressure