

## Use of Diatomaceous Earth to Accelerate Drying of Ammonium Nitrate

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The drying characteristics of ammonium nitrate prills coated with diatomaceous earth were compared to those of noncoated material using both a tray and small rotary dryer. Nitrate with 3 to 4% coating agent dried from 2.5 or 3.0% to 0.2% moisture, dry basis, in about one third the time required for noncoated material. This amount of coating agent gave the greatest increase in drying rate. The relative difference in drying rate between coated and uncoated material increased as the moisture content decreased. Air velocity had no significant effect. In the rotary dryer less fines were formed during the drying of coated material. A mechanism to account for the phenomena observed is postulated and supported by photomicrographs of individual prill cross sections.

AMMONIUM NITRATE is widely used in this country in fertilizers and as an explosive. The Stengel and conventional prilling processes are generally used in its manufacture. In the conventional prilling process the solid prills are formed from a solution containing 3 to 5% water and the resulting product is dried. If the moisture content is not reduced to a few tenths of 1% or if the ammonium nitrate later picks up water from the atmosphere, the particles cake and become unmanageable.

Removal of moisture from solid ammonium nitrate is difficult and the operation requires a series of large rotary dryers frequently supplied with specially conditioned air. Consequently the drying operation represents a significant part of the cost of manufacturing ammonium nitrate.

Van Krevelen and Hofstijzer (4, 5) have studied bulk and individual granule drying of several materials. When drying a single granule of nitrochalk (60% ammonium nitrate, 40% marl) it was found that the granule dried rapidly for the first 5 minutes (a falling rate period) and then at a lower constant rate for 4 hours before attaining the equilibrium moisture content. The constant rate of drying for nitrochalk was only 1/1500 of that for a similar completely insoluble granule dried under identical conditions.

These investigators assumed the following mechanism for the drying of a nitrochalk granule: At the outset water evaporates at a constant rate from a saturated ammonium nitrate solution supplied to the surface from the interior of the granule; next nitrate crystals deposit at the surface, gradually closing the pores through which the solution

has been flowing to the surface and thus decreasing the drying rate; finally all the pores are closed and the flow of solution to the surface is stopped. Soon the entire granule reaches the temperature of the drying air and drying at a constant but greatly reduced rate takes place by vaporization within the pores of the granule, followed by diffusion of the water vapor through the crystal "shell" at the surface.

Studying the problem of drying nitrochalk in a rotary dryer using grain sizes from about 25- to 32-mesh, the same investigators found the over-all coefficient of mass transfer for the final constant rate period to be nearly the same as that for a single granule. The reason suggested for this was that in both cases the rate-determining process was the diffusion of water vapor through the thin layer of ammonium nitrate which obstructed the pores of the granules. There is every reason to believe that these same conclusions can be used to account for the slow drying of pure ammonium nitrate.

The purpose of the present work was to learn more about a means for accelerating the drying of ammonium nitrate first reported in 1956 by Giachino (2). His invention consisted essentially of mixing a moisture-containing granular material of high moisture-diffusion resistance which was to be dried, with a water-insoluble, inorganic material—e.g., diatomaceous earth—having a large surface area, and then drying the mixture in a stream of air. This, it was reported, greatly increased the drying rate of high moisture diffusion resistance material. Results obtained by Giachino in a small rotary dryer using 3% coating agent on ammonium nitrate are shown in Table I. No work has been done by the consignee beyond that which led to the original discovery (3).

Fertilizer grade nitrate particles are normally conditioned prior to shipment or storage, by either coating or dusting with a parting agent (diatomaceous earth is most commonly used) to retard adsorption of water and reduce the effects of water which may be present. Hence incorporation of the Giachino discovery into the ammonium nitrate manufacturing process could call for no more than adding the parting agent before instead of after drying.

Diatomaceous earth is a hydrous opaline form of silica composed of innumerable skeletons of microscopic aquatic plants. Impurities include small amounts of sand, clay, calcium carbonate, magnesium carbonate, volcanic ash, and organic matter. Chemically combined water varies from 2 to 10%. The material is usually mined from a quarry or open pit, then dried, pulverized, and sometimes calcined. Table II gives the properties of the two Johns-Manville products which were used in this work as coating agents; the run of the mine material is Celite 379 and a refined product, Micro Cel E.

Table I. Ammonium Nitrate Drying Data Reported by Giachino (2)

Material	Drying Time, Min.	Moisture Content, Wt. %	
		Initial	Final
Uncoated	20	1.6	1.10
Coated	20	1.5	0.34

Table II. Properties of Diatomaceous Earth Coating Agents (1)

Properties	Micro	
	Celite 379	Cel E
Bulk density, lb./cu. ft.	8.2	5.4
Water absorption, wt. %	195	560
Surface area, sq. meters/g.	10-15	95
Av particle size, microns	0.5-1.5	2.1

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## Tray Dryer Tests

A schematic drawing of the tray dryer is shown in Figure 1. Air was partially recirculated past steam-heated coils and over the drying tray. A needle valve was used to regulate steam flow to the coils and consequently the air temperature. Pans of water were placed in the dryer to maintain a constant humidity. The drying tray was suspended by a rod from one arm of a pan balance mounted on top of the dryer. The rod passed through a small hole in the top of the dryer.

The drying tray was insulated to reduce heat transfer through the bottom and sides and sheet metal cowlings were fitted to the ends to minimize air turbulence. A wet- and dry-bulb thermometer set was used to measure the humidity in the dryer and an anemometer the air velocity over the tray.

The ammonium nitrate used was a conventional prilled product (-6+14 mesh) obtained from the Spencer Chemical Co. The material was dried prior to shipping but was not coated. To prepare test samples, moisture in the form of a saturated solution was added to dry ammonium nitrate in a small twin-shell blender. This resulted in a uniform product that gave drying curves typical of run of the plant prills and to which the coating agent was added while the moist fertilizer was still in the blender. The Karl Fischer reagent was used to determine moisture in the fertilizer both before and after drying.

To carry out a drying test the dryer was turned on and allowed to come to equilibrium. The moisturized and coated prills were placed in the tray and the tray was hung from the balance. As drying progressed, total tray weight was recorded as a function of time. For all tests the dry bulb temperature was maintained at 160° F., the wet bulb at 64° F., and the air velocity at 12.4 feet per second.

The drying rate of ammonium nitrate as a function of the amount of Celite 379 coating added was first studied. Figure 2 shows the effect of weight per cent coating on drying time, expressed as the fraction of time required to dry uncoated material under identical conditions. Data were taken for three different final moisture contents.

From these curves it can be seen that the least drying time is required (when drying from 2.5% initial moisture) for a coating level of about 3.5% by weight Celite 379. The greatest increase in drying rate occurs at the lower moisture levels. The fraction of time required to dry material from 2.5 to 0.4 or 0.5% moisture is greater than that required to dry from 2.5 to 0.2% moisture for the same amount of coating. Figure 3 shows that the increase in drying rate varies inversely with moisture content.

Similar tests were carried out using Micro Cel E, which has greater adsorptive capacity than Celite 379 and a higher surface area per gram. While

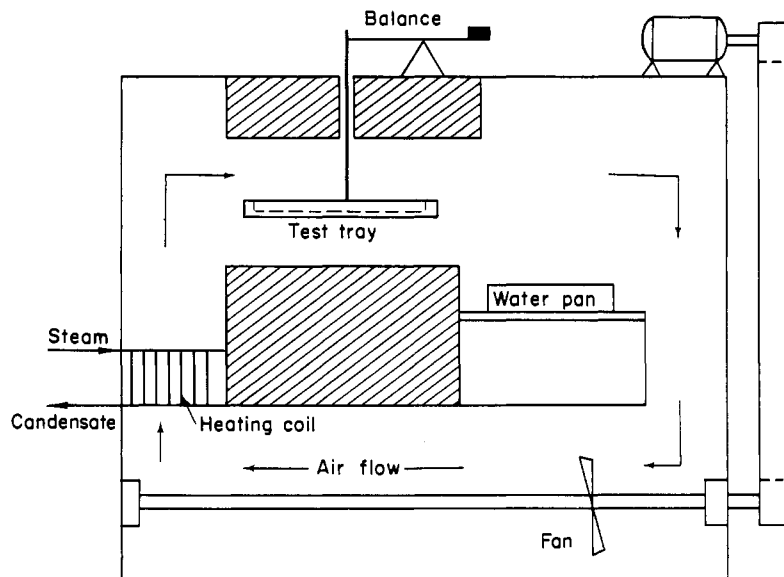


Figure 1. Schematic diagram of tray dryer

the data are not as complete for Micro Cel E as for Celite 379, Micro Cel E is the more effective agent for increasing the drying rate of ammonium nitrate (Figure 4). At 3.0% coating agent, the drying time fraction when going from 2.5 to 0.2% moisture was 0.33 for Celite 379 and 0.19 for Micro Cel E. Similar results were obtained for other moisture ranges.

In other tests the air velocity over the tray was varied while all other conditions were held constant. No change in drying time was observed, which indicated that the drying mechanism was not simply a case of surface evaporation.

## Rotary Dryer Tests

The dryer used was a Bartlett-Snow-Pacific Model T-9091 (Figure 5). It was operated in a countercurrent manner with finned steam coils used to preheat the entering air. Steam inlet valves to each of three banks of coils made possible control of the inlet air temperature for any one run to within  $\pm 0.5^\circ$  F. Two dampers controlled the air velocity from 0 to a maximum of 27 feet per second.

The dryer shell measured approximately 6 inches in i.d. by 3 feet in length. The feed end had a 1-inch retainer ring to prevent loss during charging. There were six evenly spaced flights parallel to the axis of rotation and extending halfway down the shell at the feed end, and six identical flights at the product end, the two sets of flights being offset by 30°. Wet- and dry-bulb mercury thermometer sets were used to measure inlet and outlet air temperatures.

Tests were conducted using moisturized and coated prills prepared in the same manner as those used in the tray dryer tests. All runs were made with an initial moisture content of approximately 3%, a linear air velocity of 12.3 feet per second, and a rate of rotation of 10 r.p.m.

One hour prior to a run the blower and steam to the dryer were turned on to

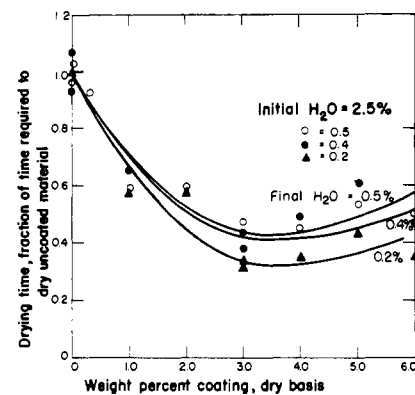


Figure 2. Time required to dry ammonium nitrate from 2.5% water for various amounts of Celite 379 coating and different final moisture contents

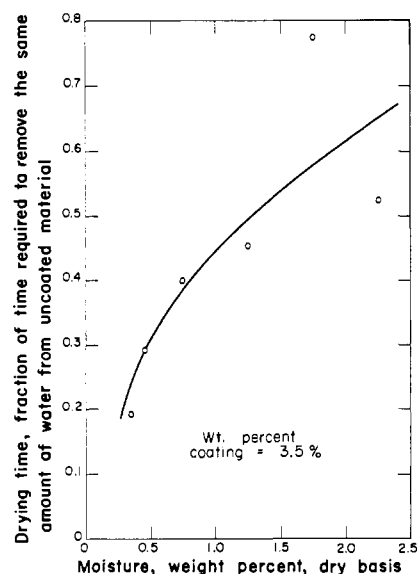


Figure 3. Incremental drying times for ammonium nitrate coated with 3.5% Celite 379 at various moisture levels

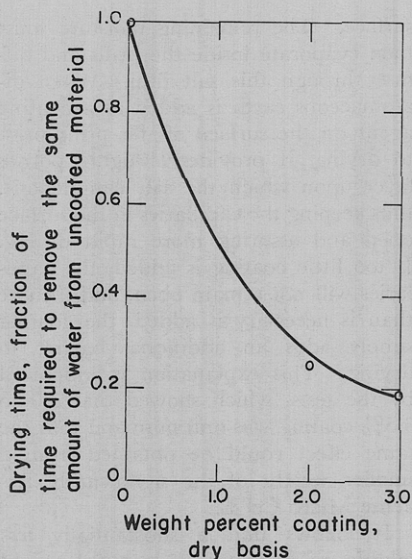


Figure 4. Time required to dry ammonium nitrate from 2.5 to 0.2% water for various amounts of Micro Cel E coating

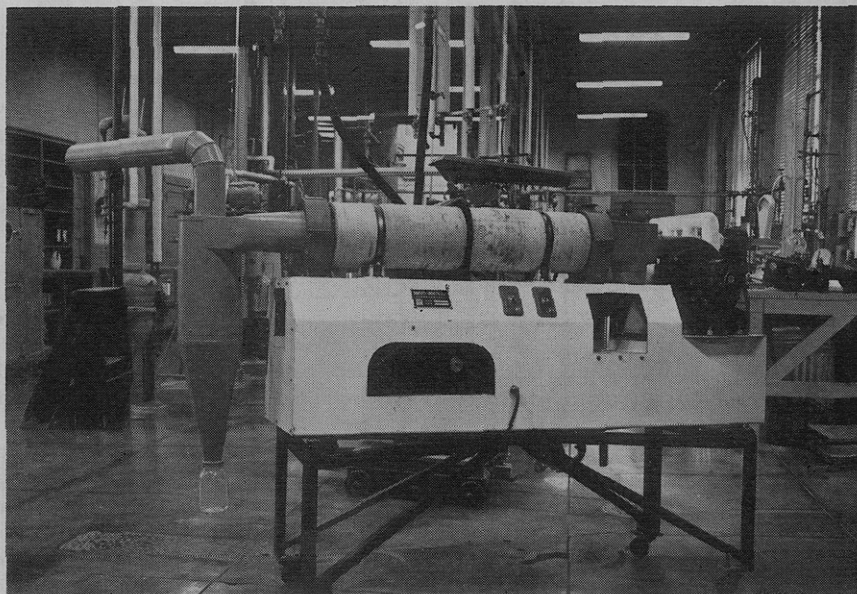


Figure 5. Steam direct-heated, countercurrent, rotary dryer

allow time to reach equilibrium and adjust the inlet air temperature. Preliminary tests were conducted in a batch manner by rapidly charging 1200 grams of prepared prills (7% of the dryer volume) to the dryer and then removing 6- to 8-gram samples periodically until the run was terminated. In no run did the total amount of material removed exceed 50 grams. The inlet and outlet air temperatures were held constant to  $\pm 1^\circ$  F.

Moisture content as a function of inlet air temperature and drying time is shown in Figure 6. From the results of these tests  $190^\circ$  F. was selected as a standard temperature at which to determine the optimum per cent coating agent. This temperature closely corresponds to that used industrially to dry ammonium nitrate prills.

Figure 7 shows the effect of per cent coating agent on moisture content. As can be seen, a 4.0% coating reduced the moisture content from 3.0 to 0.38 in 60 minutes. In the same period a 3.0% coating gave a final moisture content of

0.24%, while 2.5% coating gave 0.33%. These data indicate that approximately 3.0% coating is optimum from the standpoint of drying time required to reach a given final moisture content.

During the above rotary dryer tests it was observed that uncoated prills produced more fines during drying than did the coated material, time in the dryer being the same (60 minutes). This effect was confirmed by screen analyses of the dryer product from runs made with no coating and with 3.0% coating. Fines (-14-mesh) in the uncoated product comprised 12% by weight; for the coated material only 4%. Although "dusting" from suspended solids in the exit air stream was very slight in all tests, it was noticeably greater with the uncoated material.

This phase of work culminated in a continuous run on the rotary dryer in which the drying conditions were the same as in the batch tests. Prills were fed to the dryer at a rate that gave a residence time of 70 minutes, during

which the moisture content was reduced from 3.0 to 0.2%. Inlet air temperature was  $190^\circ$  F. and level of coating 3.0%.

#### Photomicrographs

To determine changes occurring during drying, thin sections of individual prills were prepared. Two clear glass slides, A and B, were placed in an oven at about  $140^\circ$  F. After they had reached oven temperature, a drop of thermoplastic resin was placed on each slide. Then on slide A, 15 or 20 prills were placed in the resin and that slide was removed from the oven and placed in a desiccator.

When the resin had set, the slide was removed from the desiccator and the prills were ground off to approximately their horizontal axial plane, using a rough glass plate and kerosine as a lubricating agent. Slide A was then placed back in the desiccator for a short time to allow the adhering traces of kerosine to evaporate. It was then placed face down on slide B, which was still in the oven, and pressed firmly to obtain tight adhesion. Both slides were

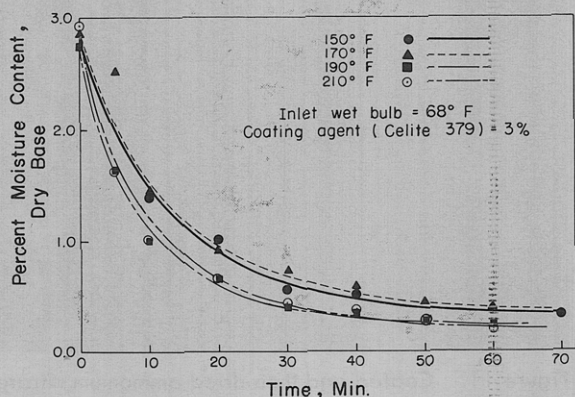


Figure 6. Effect of inlet air temperature on drying time

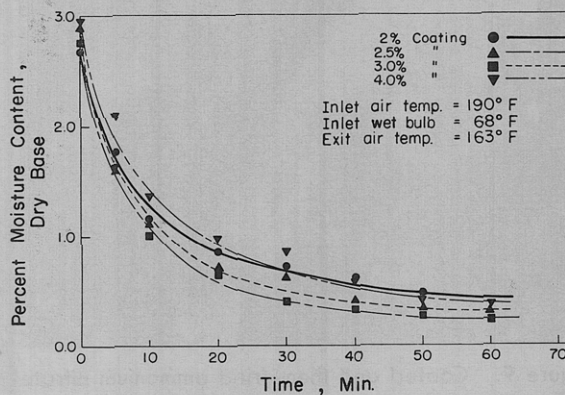


Figure 7. Effect of amount of coating added on drying time



then removed from the oven and allowed to cool.

When at room temperature, the slides were placed back in the oven with slide A on the bottom resting on a metal plate. Because A was heated faster because of conduction from the plate, it could be slid away from B with the prill "halves" remaining attached to B with their flat sides down. This slide could then be cooled and a thin section prepared by grinding the prills to a wafer with a thickness of about 30 microns. Photomicrographs were then taken using a microscope with a built-in 35-mm. camera. Magnification ranged from 25 to 600 $\times$  and fine-grain Pan-Atomic Kodak film was used.

Figures 8 through 11 are selected photomicrographs typical of those obtained from the thin sections. Figure 8 shows an uncoated, nondried prill which was hollow in the center, a condition already generally known to exist in conventional prills. A coated and dried prill is shown at somewhat greater magni-

fication (100 $\times$  in place of 50 $\times$ ) in Figure 9. The layer of coating agent is clearly discernible, as are crystals of nitrate which were deposited on the outside of the layer from solution diffusing to the surface and then evaporating. Individual nitrate crystals can be seen both within the prill and in the outer layer.

Figures 10 and 11 are of a different coated and dried prill and are at a greater degree of magnification, 160 $\times$  and 400 $\times$ , respectively. These were selected to show the dense nature of the deposited surface layer of ammonium nitrate.

As a possible explanation of the results observed, the following is proposed. It is known that uncoated ammonium nitrate prills have a very low drying rate. Apparently moisture initially leaves the individual prills by evaporation at the surface from a saturated solution which deposits a dense film of salt and blocks the limited number of capillaries to the

surface. The remaining moisture must then evaporate inside the prills and diffuse through this salt film. When diatomaceous earth is added as a coating agent on the surface of the prills prior to drying, it provides a highly porous layer upon which the salt can deposit, thus keeping the capillaries to the surface open and assuring more rapid drying. If too little coating is added, the capillaries will not remain open, and if more than is necessary is added, the coating simply adds an additional barrier to drying. This explanation is supported by the tests, which showed that 3.0 to 3.5% coating was optimum and that the same effect could be obtained from a smaller weight of the significantly less dense Micro Cel E.

It follows that a substantially less soluble or hygroscopic material would not dry faster if it were coated. This conclusion was supported by tests performed using 16-20-0 granular fertilizer, during which samples were dried

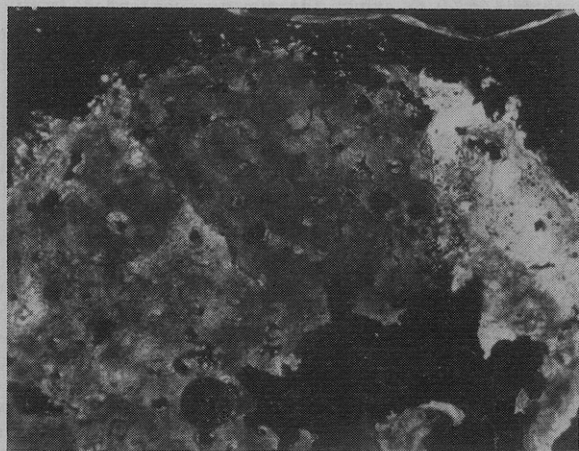


Figure 8. Photomicrograph of uncoated ammonium nitrate prill, showing hole in center of prill

50 $\times$

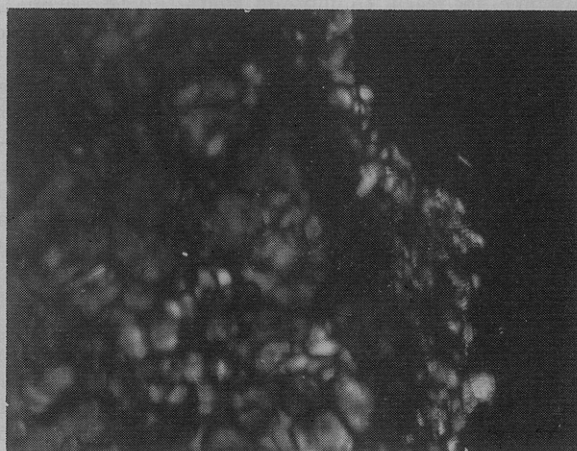


Figure 10. Coated prill showing ammonium nitrate diffused through diatomaceous earth coating during drying

160 $\times$

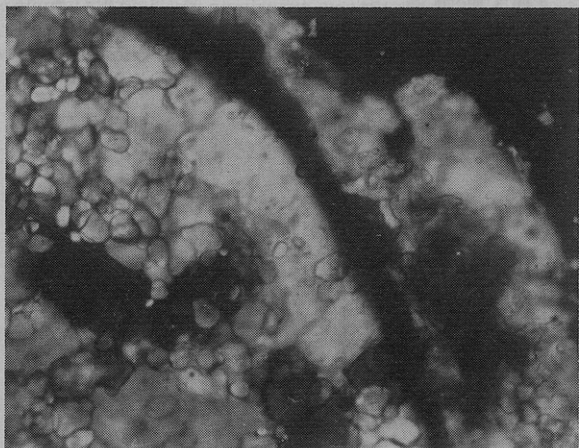


Figure 9. Coated and then dried ammonium nitrate prill

100 $\times$ . Dark curving line is layer of Celite 379 originally on outside of wet prill.

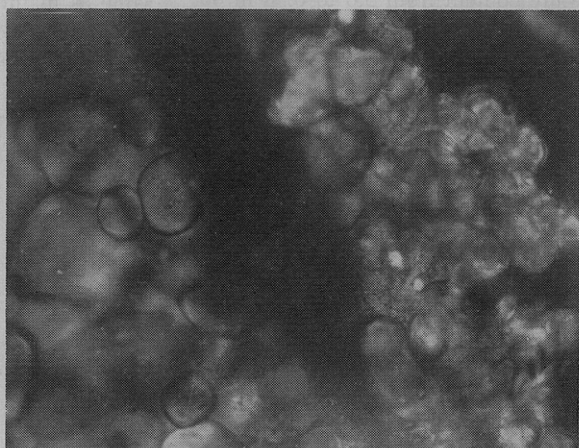


Figure 11. Coated and then dried ammonium nitrate prill

400 $\times$ . Note more dense crystalline nature of diffused ammonium nitrate at right

in the cabinet dryer from initial moisture contents as high as 5.0%. No reduction in drying rate occurred when the coating was added.

### Conclusions

Addition of diatomaceous earth as a coating agent to moist ammonium nitrate prills significantly increased the rate of drying in both cabinet and rotary dryer tests. Limited data indicated that the coating also reduced the amount of fines produced in the dryer. Photomicrographs of prill thin sections showed that a thin, dense layer of nitrate de-

posited during drying on the outside of the coating. Without the coating the deposited salts would have quickly blocked the capillaries which bring moisture to the surface. At optimum thickness, the layer of coating probably keeps the capillaries to the surface of the prill open, resulting in a shorter drying time.

### Acknowledgment

The prilled ammonium nitrate was donated by the Spencer Chemical Co. and the diatomaceous earth by Johns-Manville.

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## GOSSYPOL TOXICITY

### Effect of Cooking and Calcium and Iron Supplementation on Gossypol Toxicity in Swine

Studies were carried out to determine whether cooking and the addition of calcium and iron protect swine against gossypol toxicity. Gossypol in the diet resulted in lower weight gains and feed efficiencies and a high mortality rate. These effects were completely eliminated by the addition of 1%  $\text{Ca}(\text{OH})_2$  and 0.1%  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Serum proteins, albumin, globulin, and urea nitrogen concentration remained the same under the different treatments, but hemoglobin and hematocrit values were lower in animals fed cottonseed meal diets. Liver weight was lower in animals fed raw or cooked cottonseed meal and liver fat highest in the group fed raw meal. Histopathological studies of the heart indicated that cottonseed meal fed without addition of calcium and iron resulted in dilation of both auricles and ventricles. This lesion, of a degenerative type, which resulted in cardiac insufficiency and edema of the lungs, is probably muscular, since no abnormalities were observed in the valves.

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THE fatal outcome which often follows the prolonged feeding of large amounts of cottonseed meal to monogastric animals, but particularly to swine, is well documented (7, 28). It is also known that the adverse physiological effects of cottonseed meal are due to a large extent to gossypol (7, 8, 20, 29).

The toxicity of cottonseed meal due to the presence of gossypol can be reduced by the processing conditions used during the extraction of oil from the seed (7, 9, 13, 22). Since at the same time there is a decrease in available lysine content (4, 10, 24), the deficiency of this amino acid is further aggravated by the presence of gossypol, because it binds lysine, reducing the protein quality of the meal (24, 25). Newer developments in cottonseed processing have made possible the production of cottonseed meal practically free from gossypol (22), with minimum destruction of the protein quality.

Attention has also been given to dietary factors which reduce the toxicity

of gossypol. Hale and Lyman (14) showed that gossypol tolerance in swine could be increased by increasing the protein level in the diet. The beneficial effects of protein level in the diet have been attributed to either a higher availability of amino acids, particularly lysine, or the presence of specific components in the supplements (7, 9, 12, 16, 23). Hale and Lyman (15) also demonstrated that lysine supplementation of sorghum-cottonseed rations for swine greatly improved the daily gains and feed efficiencies despite the increased gossypol intake.

The addition of ferrous salts to diets containing cottonseed meal has been shown by Gallup (12), Barrick (5), Withers and Carruth (37), Hale and Lyman (16), and Clawson and coworkers (8) to reduce the toxicity of gossypol to varying degrees. It is believed that the beneficial effects of the added iron are due to the formation of an insoluble iron compound of gossypol and to the oxidation of gossypol, thus decreasing its

concentration. Bressani and coworkers (6) have shown recently that the addition of iron in the presence of calcium salts, with and without cooking, reduces to very low levels the concentrations of free gossypol in food mixtures containing cottonseed flour. It was, therefore, of interest to determine whether the addition of calcium and iron would protect swine against gossypol toxicity when fed a raw or cooked cottonseed meal diet with a relatively high gossypol content and to determine the biochemical and histopathological changes in the blood and organs of the animals studied.

### Materials and Methods

**Experimental Procedure.** The experiment consisted of five treatments, one of which was a control, and each treatment was replicated three times. In the first replication, 15 half-bred Duroc Jersey pigs were used, allotting three pigs per treatment, and in the second and third, 15 and 20 pure-bred