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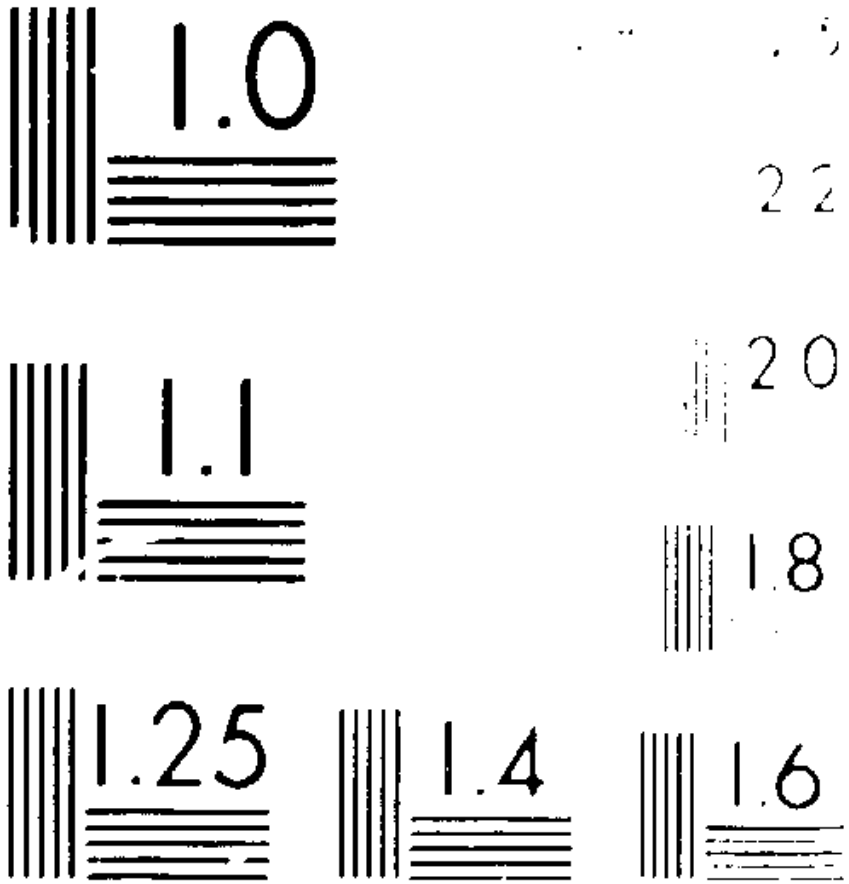
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IMPROVEMENTS ON THE QUALITY OF AMMONIUM-BICARBONATE FERTILIZER AND ITS APPLICATION*

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ABSTRACT

NH_4HCO_3 is the widely used nitrogenous fertilizer in our country. It is suitable for various kinds of soils. It has no detrimental acid ions. It has been proved effective in raising the crop yield.

However, NH_4HCO_3 has its inherent shortcomings: low nitrogen content, easy to decompose and volatize, high water content and easy caking tendency.

These cause a lot of difficulties in production, transport, storage and application.

In recent years, various measures have been taken by our manufacturers to improve the quality of NH_4HCO_3.

Certain chemical additives are effectual for enlarging the crystal size, lowering the water content, decreasing the decomposition loss and even preventing the caking of NH_4HCO_3 fertilizer.

Pressed pellet-form of NH_4HCO_3 exhibits fine properties appropriate for mechanical and deep dressing.

Hot-air-dried NH_4HCO_3 enhances its chemical stability.

All these modifications improve the product properties to a certain extent.

Extensive work done by many institutes of agricultural science on the evaluation of NH_4HCO_3 as a nitrogenous fertilizer has shown that its effectiveness is about the same as that of other nitrogenous fertilizers in the case of deep dressing.

Therefore it is justified to produce NH_4HCO_3 for local consumption in small-size plants.

1. Introduction:

The ammonium bicarbonate fertilizer is fit for prolonged use in various soils without the risk of hardening the latter. Crops may take up both ammonia and carbon dioxide from ammonium bicarbonate fertilizer simultaneously without leaving harmful substances in the soil. If appropriate application techniques, such as deep placement, are used, its effectiveness can equal that of ammonium sulfate of equivalent nitrogen content. But on account of its low nitrogen content, packaging and transportation per ton of nitrogen are more expensive. Besides, its additional properties of high moisture content, easy decomposition and strong caking tendency make it inconvenient for application.

To bring the effectiveness of ammonium bicarbonate

into full play, it is necessary to improve its physical properties, so that convenient use and less loss are ensured. Taking these characteristics of bicarbonate into consideration, deep dressing is required in order to maximize the utilization of its nitrogen nutrient.

II. Physicochemical characteristics of ammonium bicarbonate:

1) Decomposition reaction of ammonium bicarbonate:

The pure ammonium bicarbonate may decompose at the atmospheric pressure and ambient temperature according to the following equation:

$$NH_4HCO_3 = NH_3\ (g) + CO_2\ (g) + H_2O\ (g)$$

The partial pressure of each component in equilibrium at 25°C can be calculated thermodynamically. The sum of partial pressure of NH_3, CO_2, H_2O amounts to 0.054 atm., which is in good agreement with observed values (experimental value at 25.4°C 59 mm Hg.).

2) The vapor pressure of ammonium bicarbonate:

Ammonium bicarbonate is characterized by a vapor pressure rising with increasing temperature and water content. The vapor pressure observed in experiments is listed below (Tab. 1 and 2).

3) Weight loss rate of ammonium bicarbonate in air:

The weight loss rate of ammonium bicarbonate was measured at 3[illegible] °C and a relative humidity of 69%(Tab.3).

The decomposition of ammonium bicarbonate in air depends on temperature, air humidity and moisture in sample. In case of relatively low ambient temperature and moderate air humidity, the NH_4HCO_3 exposed to air undergoes a rapid loss in weight at the initial stage due to decomposition and hrying. The rate at which the weight is lost slows down gradually as the sample becomes dried. At higher air humidity and ambient temp.. ammonium bicarbonate forms a film of saturated solution by absorbing moisture from air. The decomposition of ammonium bicarbonate is accelerated, because of the partial pressure of NH_3 over the saturated solution being greater than that of soild ammonium bicarbonate. Evolution of ammonia and carbon dioxide is accompanied with buildup of water. Consequently, such a vicious circle leads to a complete deliquescence of ammonium bicarbonate crystals. Hence, the primary measures to be taken to stabilize the bicarbonate are to reduce its moisture content and its hydroscopicity . Ammonium bicarbonate should be air-tightly stored and kept free from water. It should be pointed out that properly packed ammonium bicarbonate is practically not subject to any loss. The loss measured during piling is less than 1%.

Tab. 1 Vapor pressure of ammonium bicarbonate

Temperature, °C	25.4	34.2	40.7	45.0	50.0	50.8	54.0	55.8	59.25
vapor pressure (mm Hg)	59	122	201	[illegible].5	395	423	541.5	615.7	815.0

Tab. 2 Vapor pressure of ammonium bicarbonate with different moisture contents

Temperature, °C	25	30.8	37.1	43.2	48.9	54.9	57.9
vapor pressure of dry salt(mm. Hg) moisture 0.16%	60.6	97.6	159.6	240.1	378.9	584.1	725.9
vapor pressure of wet salt (mm Hg), moisture 5.37%	90.1	145.1	237.3	371.8	555.9	760.0	

Tab. 3. Weight loss of ammonium bicarbonate in air

Time (hour)	4	8	12	20	24
Dry salt weight loss (%), containing a moisture of 0.5%	0.58	1.23	1.84	2.98	3.64
wet salt weight loss (%) containing a moisture of 4.34%	18.3	36.63	57.41	84.88	86.00

III. Several approaches for improving the quality of ammonium bicarbonate:

It is evident from its chemical properties that ammonium bicarbonate as a nitrogen fertilizer suffers from three drawbacks: firstly, chemical instability and easy decomposition; secondly, low nitrogen content and expensive transportation; finally, fine crystal, high moisture, readily caking, poor physical properties and inconvenient use. Thus far three methods have been adopted at present in ammonium bicarbonate plants to improve the product quality.

1) Chemical additives:

Numerous studies with various additives such as mineral salts, oils, organic compounds and surfactants have been done to minimize the loss of ammonium bicarbonate due to decomposition. These additives are introduced either after or prior to the crystal growth of the bicarbonate. In the former case the additive is spread over the bicarbonate crystals by spraying or washing, while in the latter case it is added to the solution.

It has been found out through the experiments that by addition of anionic surfactant into the aqueous ammonia solution, coarse crystals may be obtained after carbonation, enabling the moisture in wet bicarbonate

product to be reduced from about 5% to about 3.5%, resulting in less decomposition loss and bringing about remarkable anticaking effect. This method has been adopted in more than 100 fertilizer plants in our country.

The essential effect of additives is to increase the dimension of bicarbonate crystals. We think that in the presence of a given amount of additive some colloid bundles may be formed and dispersed in the aqueous ammonia solution, as soon as a critical concentration of colloid bundles is reached. As it is well known from the characteristics of anionic surfactants all the hydrophilic groups attached to the surface of colloid bundles are anions, adsorbed by equal number of NH_4^+. In the solution as a whole, the NH_4^+ ion concentration in the vicinity of colloid bundles is higher than that in the solution proper; formation of bicarbonate takes place preferably in regions where the NH_4^+ ion concentration is high, crystal nucleus also forms first in the vicinity of colloid bundles. A given concentration of additive in aqueous ammonia relates to the numbers of colloid bundles formed. Subsequently, the number of crystal nucleus, is governed by that of colloid bundles. Considering the course of crystallization as a whole, crystal size is influenced by a lot of factors, viz. The operating temperature, temperature profile of carbonation tower, gas velocity, aging time for crystals, impurities in aqueous ammonia, etc. All these factors contribute to the rate of nucleus formation and the rate of crystal growth.

For a given output, coarse crystals may be obtained if the nucleus formation rate is less than the crystal growth rate. With the introduction of additives, the number of crystal nucleus formed becomes less than that without additives, and therefore the crystals grow larger.

Coarse grains which are readily separable contain less moisture and require less package expenses due to the increased bulk density. The decrease in moisture content contributes to the reduction of decomposition rates of bicarbonate. Experimental data show that the decomposition rate of bicarbonate with and without additives differed considerably (Tab. 4).

The anticaking effect of additives is due to the layer of surfactant adsorbed on crystal surfaces which inhibits the crystals from bridging and agglomeration.

The recommended additives are alkylsulfonates or alkylbenzosulfonates, their dose varies from 0.1-0.01%.

2) <u>The press pelletizing of ammonium bicarbonate:</u>

The bicarbonate can be upgraded by pelletizing. The pelletized product, being more resistant to caking, is suitable for mechanical deep dressing. Since the specific surface area of granular fertilizer is significantly reduced as compared with powder fertilizer, it is subject to less volatilization loss.

The press machine is composed of a pair of stainless steel clad rollers with a large number of nests, flat in shape and Ø12.5mm x 3.4mm in size, arranged over their surfaces. The press machine has a throughput of 4-6 tons/hr., each pellet weighing 1 g.

3) Drying:

What mentioned above describes that the moisture accounts for decomposition of bicarbonate and the drying of wet material would be an effective means to raise its stability. In common practice, hot air drying is used and the moisture is swept out with hot air. As a result of our experiments, we think the product qualities can be improved, if both drying and additives are used in combination.

IV. Evaluation of the effectiveness of ammonium bicarbonate:

1) State of nitrogen supplied by NH_4HCO_3:

Ammonium bicarbonate is an ammoniacal nitrogenous fertilizer, characterized by its tendency to decompose into ammonia, carbon dioxide and water. When applied on the surface layer of soil, the ammonia evolved from decomposition partly escapes into the atmosphere and partly diffuses into the water film over soil particles and adsorbed in the form of ammonium ions. When

Tab. 4. The comparison of decomposition loss of ammonium bicarbonate with or without additives

(exposure to air, environment temp. 18–23°C)

Samples	Moisture content %	Sample weight (g)	After 1 day	After 2 days	After 3 days	After 4 days	After 5 daya
without additive 1	5.64	15.00	12.03	9.76	7.59	5.20	5.02
2	5.30	15.00	12.20	9.54	8.67	8.61	8.53
with additive 3	3.39	15.00	13.11	12.62	12.29	12.26	12.22
4	2.60	15.00	13.66	12.33	12.30	12.28	12.24
5	2.20	15.00	14.24	14.23	14.20	14.18	14.15

deeply dressed in subsurface layer of soil, the ammonium bicarbonate repidly dissolves in soil solution with formation of ammonium ions, thus the dissipation loss is reduced. This ammoniacal nitrogen can be taken up directly by crops and mirco-organisms or adsorbed by soil colloid. Therefore the ammonium bicarbonate supplies nitrogeneous nutrient in form of ammonium ions to the crops, as shown in following equations:

$$NH_4HCO_3 \longrightarrow NH_3 \uparrow + CO_2 \uparrow + H_2O$$

$$2\,NH_4HCO_3 + \text{Soil colloid Ca} + \text{soil colloid } NH_4 + Ca(HCO_3)_2$$

2. <u>The adsorption of ammonium bicarbonate by soil</u>:

Simulation tests with 3 kinds of soil from the suburban counties of Shanghai have been carried out by the Institute of Soil and Fertilizers of Shanghai Academay of Agricultural Science (Tab. 5). Under ordinary dressing conditions of ertilizer, the adsorption of ammonium bicarbonate on soil amounts to about 110% of ammonium sulphate.

The carbon dioxide constituent in ammonium bicarbonate is needed by photosynthesis. In addition, the ammonium bicarbonate contains no other harmful constituents so that there is no harmful effect on soil even for long time dressing.

3. The effectiveness of ammonium bicarbonate :

Since China used ammonium bicarbonate as nitrogenous fertilizer in 1958, extensive experiments have been carried out by institutes of agricultural science at many places. It has been proved that ammonium bicarbonate, like other nitorgenous fertilizers, shows remarkable yield-increasing effect on various soils and crops.

1) Ammonium bicarbonate has shown satisfying effectiveness in increasing yields for majority of crops. The effectiveness of this nitrogen fertilizer for wheat, maize, millet, sorghum, rice, sweet potato, cotton and other crops can be illustrated by experiments conducted by the Shandong Province Institute of Soils and Fertilizers, Academy of Agricultural Science(Tab.6).

2) Comparison of ammonium bicarbonate with other nitrogenous fertilizers:

These showed the fertilizer effect of ammonium bicarbonate was slightly below that of ammonium sulphate and urea, and comparable to that of ammonium chloride and ammonium nitrate (Tab. 7). Comparing the effectiveness of bicarbonate with that of other nitrogen fertilizers, it is found that the values of significance of difference both for bicarbonate: ammonium sulphate and bicarbonate: urea attain the most significant level ($t > t\ 0.01$). It is also found that the values of significance of difference both for ammonium chloride

Table 5. The adsorption of Ammonium Bicarbonate and Sulphate by 3 kinds of soil from the suburban counties of Shanghai

Kinds of soil	Adsorption of ammonium bicarbonate, %	Adsorption of ammonium sulphate, %	Adsorption of ammonium bicarbonate relative to ammonium sulphate
Huangjiasha Soil	95.45	86.10	111
Gouhan Soil	97.06	90.70	107
Qingzi Soil	96.10	86.60	111

By courtesy of the Institute of Soils and Fertilizers under Shanghai Academy of Agricultural Science (1973)

and ammonium nitrate are under the level ($t < t_{0.05}$).

4. Application methods of ammonium bicarbonate:

When ammonium bicarbonate was applied into the subsurface layer, besides promoting the adsorption of ammonia by soil, it also helped the process of its dissociation into the ammonium ion and bicarbonate radical, with the result that nitrogen volatilization loss was reduced, air pollution decreased and roots extension promoted. And in paddy fields the loss caused by nitrification and denitrification is lessened, because ammonium ion is in the anaerobic condition.

The simulated experiment on deep dressing of ammonium bicarbonate in medium loam with 13.6% moisture at a temperature of 29°C, which was carried out by The Soil and Fertilizer Research Institute of Shandong province, showed that the nitrogen nutrient loss was great in surface dressing, and the volatilization loss was reduced a great deal, when it was applied at a depth of 6-10cm (Tab. 8).

1) Deep application of powdered ammonium bicarbonate:

Field test of over 600 experiments carried out by the Shanghai Agricultural Scientific Academy in the suburbs of Shanghai from 1971 to 1978, showed that the rice yield by adopting deep application in thw whole plough layer was 10% higher than by adopting surface dressing, when

Tab. 6. Effect of NH_4HCO_3 on the increase in crop yield

Crops	Number of experiments	Increase in yield (kg)/NH_4HCO_3(kg)		Increase in yield (kg)/ Nitrogen nutrient (kg)	
		range	average	range	average
Wheat	22	1.36-3.66	2.59	8.69-22.8	16.19
Maize	25	1.70-5.12	3.59	10.63-32.00	22.44
Millet	8	1.69-4.20	3.07	10.56-26.25	19.19
Sorghum	3	1.22-2.14	1.58	7.63-13.38	9.88
Rice	3	1.53-4.41	2.71	9.56-27.56	16.94
Sweet potato	6	14.70-60.10	34.00	91.88-375.63	212.5
Cotton	7	1.25-1.91	1.40	7.81-11.94	8.75

Table 7. The comparison of fertilizer effects between ammonium bicarbonate and other nitrogenous fertilizers

Materials	Number of experiments	Average yield increased(%)	Increase or decrease percentage frequency					
			90	90 - 94.9%	95- 99.9%	100- 104.9%	105- 109.9%	110%
ammonium sulphate	48	4.84	0	1	11	17	8	11
Urea	31	3.94	0	1	9	12	4	5
ammonium chloride	29	2.18	4	0	6	6	8	5
ammonium nitrate	36	2.60	1	8	5	11	3	8

* by taking the yield when applying ammonium bicarbonate as 100%

equal amount of ammonium bicarbonate is used. For deep application in the whole plough layer, before transplanting double-cropping rice, 80% ammonium bicarbonate was distributed in the fields after irrigation and harrowed into the plough layer, while the rest was used as top-application. For surface dressing, 40% ammonium bicarbonate was spread on the surface as basal manure, 60% was used as top-application at two periods. The Shanghai Agricultural Scientific Academy and the Agricultural Scientific Academy of Hunan Province used 15N as the tracer to study the influence on the absorption of nitrogen by rice, employing both deep and surface dressing of ammonium bicarbonate. The results showed that the nitrogen utilization of deep application of the whole plough layer was 4.2-20.5% higher than that of surface dressing. All the above-mentioned experimental results indicated that deep application of the whole plough layer was an economical and effective method for increasing the utilization of nitrogen and rice yield (Tab. 9 and 10).

2) <u>Deep application of granulated ammonium bicarbonate:</u>

Two kinds of granulated ammonium bicarbonate have been produced. One kind, with each granule weithing about 1 g is granulated by pressing ammonium bicarbonate powder directly. An increase in yield of 8.3 - 17.2% by using granulated ammonium bicarbonate (deep application) over that by using powder (surface dress-

Table 8. Nitrogen nutrient loss of NH_4HCO_3 applied in different depths

Time	surface dressing		applied in depth of 6cm		applied in depth of 10cm	
	accumulative total loss (mg)	loss rate (%)	accumulative total loss (mg)	loss rate (%)	accumulative total loss (%)	loss rate (%)
1 day	137.81	8.35	7.90	0.48	8.11	0.49
5 days	227.17	13.77	13.70	0.83	14.64	0.89
15 days	262.57	15.91	22.77	1.38	18.84	1.14

ing) was proved in various experiments carried out by provincial or regional agricultural scientific academies (see Table 11).

Another kind of granulated fertilizer is produced by mixing a certain amount of air-dried fine clay with powdered ammonium bicarbonate and by pressing afterwards. Each granule weighed 6-10 g. Sometimes superphosphate, ground phosphate rock, pesticides or organic fertilizers can also be added. It is generally used for topdressing of rice by means of deep layer hole application. As compared with surface dressing of powdered ammonium bicarbonate, deep application of granulated ammonium bicarbonate brought an increase in rice yield of 645kg/ha (average), an increase of 14.8%, as calculated from results of 38 experiments conducted by Agricultural Scientific Academy of Fujiun Province in 1973, an increase in rice yield of 622.5kg/ha (average), an increase of 13.3% from 122 experiments in 1974. 15 more experiments carried out in the Guangxi Zhuang Autonomous Region in 1975 showed that the average rice yield increase was 741.8kg/ha, an increase of 17.8% by adopting deep application of granulated ammonium bicarbonate. And in Yunnan Province, experimental results again proved that deep application of granulated ammonium bicarbonate made rice yield increase 450-1185kg/ha, an average increase of 12.1%.

Table 9. Comparison of utilization of powdered ammonium bicarbonate when employing deep application and surface dressing

Application method	early season rice		late season rice	
	nitrogen utilization (%)		nitrogen utilization (%)	
	field	pot culture	field	pot culture
Surface dressing of basal + top-application	14.0 14.9	14.2	10.8 22.7	19.7
Basal whole plough layer (80%) + top-application	24.7 25.0	18.4	17.6 29.9	40.2

(Shanghai Agricultural Scientific Academy 1974-1977)

Table 10. Influence of different application methods on absorption of nitrogen in ammonium bicarbonate by rice

(field-simulating pot culture experiment)

Application method	absorbed and utilized by crop (%)	fixed by soil (%)
surface dressing of basal manure + top-application, twice	14.27	37.23
one time, whole plough layer application for basal manure	23.45	42.69

(Agricultural Scientific Academy of Hunan Province)

Table 11. Comparison of fertilizer effect of granulated ammonium bicarbonate by deep application and powdered ammonium bicarbonate by surface dressing

area	number of experiments	crops	average yield(kg/ha) by using powdered fertilizer	average yield(kg/ha.) by using powdered fertilizer	increase rate (%)	increase in yield (kg), granule/powder
Shandong	9	wheat	4299.0	4664.3	8.5	1.4
Shaanxi	25	rice	5550.0	6262.5	12.8	2.0
Jiangsu	14	maize	3675.0	4113.0	11.9	1.53
Guangdong	44	rice	4626.8	5016.6	8.4	1.15
Anhui	11	rice	5160.0	6048.0	17.2	2.21
Jiangsu	10	sweet potato	22067.3	23909.3	8.3	6.72

Deep application of granulated ammonium bicarbonate can raise the nitrogen utilization degree by crops. The nitrogen utilization comparision experiments between deep application of granulated ammonium bicarbonate and surface dressing of powdered fertilizer conducted by the Nanking Institute of Soil Science, Academia Sinica with 15N tracer showed that the utilization degree of the former was 23-51% higher than that of the latter, and 9-38% higher than that of surface dressing of powdered ammonium sulphate. The results indicated that the nitrogen utilization of ammonium bicarbonate was comparatively high, if a proper application method was adopted (Tab. 12).

The granulation of powdered ammonium bicarbonate by compaction not only improves the property of ammonium bicarbonate but also fully utilizes its advantages of slow-release, constance and long durability. And all these enhance its nitrogen utilization and make mechanical placement convenient. The granulated fertilizer is mainly used in paddy-fields for top-application either manually or mechanically. One granule is put for every two or four rice stands in a depth of about 5cm. Because the fertilizer effect of deep application of granulated ammonium bicarbonate is 20 days longer than that of surface dressing of powdered ammonium bicarbonate, it should be applied with right quantity at the right moment, to avoid delayed maturity and delay of next crop plantation. Large granular clay-mixed ammo-

Tab. 12. Nitrogen utilization comparision between deep application of granulated ammonium bicarbonate and surface dressing of powdered fertilizer

application methods	nitrogen utilization ratio of wheat (%)		nitrogen utilization ratio of rice (%)	
	small plot in field	pot culture	small plot in field	pot culture
powdered ammonium bicarbonate, surface application as top-dressing	19.4	36.1	31.2	27.9
granulated ammonium bicarbonate, deep application as top-dressing	56.2	71.4	54.7	78.8
ammonium sulphate surface application as top-dressing	35.6	62.1	38.9	40.9

Nanking Institute of Soil Science, Academia Sinica in 1977

nium bicarbonate is not suitable for long period storage and requires a great deal of clay, thus the extra work in fetching clay and transporting it is increased. The granulated ammonium bicarbonate by compacting powdered ammonium bicarbonate directly is not liable to cake or break easily after long period storage.

Granulators and deep dressing machine of powdered ammonium bicarbonate have been developed on a trial basis. There are tow types of granulators, one with a capacity of 4-6t/h and the other with a capacity of 1 t/h. (each granule weighs 10 g) or with a capacity of 0.6t/h. (each granule weighs 6 g). For the granulation of ammonium bicarbonate, a moisture of about 4-5% is required, otherwise the granules can not be formed and loosened from the molds. The single-row type and semi-bucket type granulated ammonium bicarbonate deep applicators, both with a capacity of $\frac{1}{15}$ ha/h for paddy-fields and plains, are all in production. There is still room for improvement for these dressing machines, such as improving the uniformity of distribution and checking the tendency of wheels to skid in deep mud.