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"STUDY AND EVALUATION OF HYGROSCOPIC BEHAVIOR OF PHOSPHATIC FERTILIZERS, AMMONIUM NITROPHOSPHATE (ANP) AND CALCIUM AMMONIUM NITRATE (CAN) BY USING DIFFERENT ANTI CAKING AGENTS, AT 80/90 % RH."A CASE STUDY AT G.N.F.C.

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Le comportement hygroscopique est le degré par lequel un produit absorbe l'humidité de l'atmosphère. Tous les engrais sont peu ou solubles dans l'eau. L'importance de l'hygroscopicité d'engrais ANP/CAN peut être mesurée par la détermination de différentes caractéristiques hygroscopiques. Pour une fluidité aisée en cours de manutention et d'application sur le terrain, il ne doit pas y avoir de prise en main en cours de formation des granules d'engrais. Aussi, les engrais ANP/ CAN sont enrobés avec différents agents antimassants. Cet exposé décrit en détail (1) les facteurs agissant sur l'hygroscopicité, (2) la détermination de l'importance de l'hygroscopicité, (3) l'évaluation des différents agents antimassants au point de vue efficacité de l'enrobage à 80-90% RH dans un local humide.

L'hygroscopicité est le degré auquel un matériau absorbe l'humidité de l'atmosphère. L'hygroscopicité de l'atmosphère est importante lorsqu'on considère (1) les conditions dans lesquelles un tas en vrac peut être stocké et (2) la fluidité dans la manutention et l'application au champ. Les déterminations d'humidité sont faites de (1) le taux d'absorption d'humidité par une unité de surface exposée, (2) la profondeur de pénétration de l'humidité (humidification visible), (3) la rétention de l'humidité et (4) l'intégrité de granules mouillées et formation de prise en masse à travers le lit de granules.

SUMMARY

Hygroscopic behaviour is the degree to which a material will absorb moisture from the atmosphere. All fertilizers are soluble in water to some extent. The extent of hygroscopicity of ANP / CAN fertilizers can be measured by determination of different hygroscopic characteristics. For easy flowability during handling and field application, there should not be cake formation in the granules of a fertilizer. So ANP/CAN fertilizers are coated with different anticaking agents. This paper describes in details (1) Factors affecting hygroscopicity (2) Determination of extent of hygoscopicity and (3) Evaluation of different anticaking agents coating effectiveness at 80 and 90 % RH in a humidity cabinet.

Hygroscopicity of fertilizers is important when considering (1) Conditions under which a bulk pile can be stored and (2) Material flowability during handling and field application. Hygroscopicity determinations are made of (1) Rate of moisture absorption per unit of exposed surface (2) Depth of moisture penetration (visible wetting) (3) Moisture holding capacity and (4) Integrity of the wetted granules and caking formation across the granules bed.

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1. INTRODUCTION

Fertilizer materials vary in their ability to withstand physical deterioration (wetting and softening),when exposed to humid atmosphere. Most fertilizer grades are hygroscopic to some extent, as well as, the fertilizers have an affinity for water as they are at least partly water soluble. Fundamentally one can expect a correlation between hygroscopicity and P_2O_5 water solubility, as a higher water solubility may be taken an indication for higher affinity of the fertilizer grade for water i.e. for an increased hygroscopicity.

- Nitrophosphates normally have a water solubility in the range of 60-80 % P_2O_5 (expressed as percentage of total amount of P_2O_5)
- The more hygroscopic a fertilizer is, the more one can expect problems during storage and handling, particularly under humid conditions. Hygroscopicity is affected by many factors such as :

  (i) Chemical composition of the fertilizer
  (ii) Moisture content
  (iii) Ambient temperature
  (iv) Relative humidity
  (v) Particle structure and porosity
  (vi) Exposure timing
  (vii) Particle surface area.

2. APPARATUS

1. Humidity cabinet
The humidity cabinet is from Metrox, model no.506. The cabinet has forced air circulation, with internal dimensions approximately 60 cm wide x 60 cm deep and 60 cm height and temperature range from 5^oC to 40^oC, and relative humidity range is 45 %- 98 %.

The temperature (30^oC) and relative humidity(80 and 90% RH) in the cabinet, is controlled by a humidity electronic controller to the range of $\pm$0.1 %, through censor, which is placed inside the humidity cabinet. The maximum variation in the humidity in the cabinet is observed $\pm$2.0%. The detail of electronic circuit of the Humidity Electronic Controller is shown in Figure 1.

2.Glass cylinder (Glass jars)
This is shown in Figure 2. The glass cylinder has a 6.8 cm diameter, and is 20 cm deep.

3. Balance
Top loading electronic balance with maximum 2 kg capacity and a resolution of 0.1gm.

3. CRITICAL RELATIVE HUMIDITY

The critical relative humidity (CRH) of the fertilizer material is defined as the relative humidity of the surrounding atmosphere (at certain temperature) at which the material begins to absorb moisture from atmosphere and below which it will not. Chemically, the critical humidity of a salt is that humidity of air at which the partial vapour pressure of water in the air exactly equals the equilibrium water vapour pressure above a saturated solution of the salt at any given temperature (e.g.30^oC).

In case the relative humidity of the atmosphere corresponds precisely to the CRH of a fertilizer such as ammonium nitrate, the fertilizer sample will take water until all fertilizer salt is dissolved to yield a saturated solution. The above considerations hold true for single nutrient fertilizer, such as ammonium nitrate, CRH 59.5% and urea, CRH 72.5% at 30°C, while mixed or multi nutrient fertilizers e.g. ANP exhibit quite a different hygroscopic behavior than the above single nutrient and from a chemical point of view single component fertilizers. These mixed fertilizers normally contain varying amounts of water soluble and water insoluble components such as $NH_4H_2PO_4$ (mono-ammonium phosphate, soluble), $(NH_4)_2HPO_4$ (diammonium phosphate, soluble), NH_4NO_3 (ammonium nitrate, soluble), $CaHPO_4$ (dicalcium phosphate,insoluble), $FePO_4$ and $AlPO_4$ (iron and aluminum phosphate, insoluble). In establishing the hygroscopical nature of fertilizer grade, the exact determination of critical relative humidity is often of no importance. More significant is the rate at which the fertilizers take up water as a function of temperature and relative humidity. This is normally measured as the increase in weight of certain sample, over time under constant conditions.

Determination of CRH is necessary when controlled humidity of storage areas are being designed for a material. The value is of interest also as an indication of the degree of protection that is likely to be required during handling. In the case of mixtures, determination of CRH is a check of compatibility. Some mixtures have an unusually low CRH, much lower than the CRH of either component alone (see 8 and 9 in Table 1).

The critical relative humidities of some pure salts and mixtures at 30°C is given below.

Table 1

	Fertilizers	% Critical relative humidity (CRH)
1.	Urea	72.5
2.	Ammonium nitrate	59.5
3.	Ammonium chloride	77.2
4.	Calcium nitrate	46.7
5.	Diammonium phosphate	82.5
6.	Monoammonium phosphate	91.6
7.	Monocalcium phosphate	93.6
8.	Calcium nitrate + Ammonium nitrate	23.5
9.	Ammonium nitrate + Ammonium chloride	18.1
10.	Ammonium nitrophosphate	58.0
11.	Single super phosphate	>90.0

The critical relative humidity would determine whether or not moisture will be absorbed under given conditions. However, it does not indicate how well or how poorly the fertilizer will tolerate the absorbed moisture. Other tests like moisture absorption, moisture penetration, flow ability and moisture holding capacity are necessary for full evaluation.

DETERMINATION OF HYGROSCOPIC BEHAVIOUR OF ANP AND CAN, BY FOLLOWING HYGROSCOPIC CHARACTERISTICS

1. Moisture absorption.
2. Moisture penetration.
3. Moisture holding capacity
4. Caking tendency.

1. MOISTURE ABSORPTION

The principle of the test is simply to expose a bulk fertilizer surface of known area to moving air at controlled temperature and humidity and to measure the rate of moisture absorption per unit of fertilizer surface, into the bulk of fertilizer. Open top glass jars with 6.8 cm in diameter, and 20 cm deep are used and the exposed surface is 36.3 cm^2.

Procedure :

The uncoated and coated samples of ANP are filled in all glass jars up to particular height for uniform distribution of humid air in humidity cabinet, since vigorous air flow across the top of the jars is important. The filled jars are weighed accurately and than are exposed in a controlled humidity cabinet at 80/90 % RH and 30^oC.

The sample jars are removed from the humidity cabinet for weighing and examinations, after a period of 4,8,24,48,72 and 96 hrs.

The samples are weighed and weight gain is calculated and expressed as milligrams/square centimeter of exposed surface as under :

$$\text{MA,mg/cm2} = \frac{FW - OW}{ES} \times 1000$$

where MA = Moisture absorption, mg/cm^2 FW = Final weight of sample, gm
OW = Original weight of sample, gm ES = Exposed surface, cm^2 = ? r^2 = 36.3 cm^2

The values of moisture absorption are shown in Figures 3-6 at 80 % RH and in Figures 7-10 at 90 % RH with 0.05% / 0.1% coating of different anticaking agents against uncoated ANP / CAN products

2. MOISTURE PENETRATION

Procedure :

The glass jars are filled with the samples leveled with a straight edge, and tapped several times on rubber sheet base, to remove the air from the granule bed. The void created by tapping is then filled with the sample and leveled up to straight edge. This is repeated until a void is no longer created by tapping. The sample is now exposed to a constant temperature 30 °C and humidity at 80 /90 % RH, for 96 hrs in humidity cabinet.

The depth of moisture penetration is measured in centimeters by observation through the colour (side) wall of the jars. Result are shown in Table 2(A) at 80 / 90 % RH with 0.05 / 0.1 % coating. The experiment was run for 96 hours.

Additionally, granule integrity is determined qualitatively by handling the surface position of the sample and reported as excellent, good, fair and poor. The results are shown in Table 2(B).

Table 2 (A) : Moisture penetration (in cm)

ANP PRODUCT		**0.05% ACA Coating**			**0.01% ACA Coating**		
	Uncoated	**A**	**B**	**C**	**A**	**B**	**C**
AT 80% RH	1.6	1.2	1.0	1.0	1.4	1.3	1.2
AT 90% RH	2.6	2.1	1.9	1.8	2.5	2.4	2.4

Sample A and B are liquid and sample C is semisolid anticaking agents

CAN PRODUCT :
Since the granules geometry of CAN product can become disturbed, due to leach out of ammonium nitrate from CAN granules, under humid condition. It is not possible to measure exact moisture penetration through granules bed.

Table 2(B) : Granule integrity of ANP/CAN uncoated and coated granules

	ANP Granules		**CAN Granules**	
	80% RH	**90% RH**	**80% RH**	**90% RH**
TOP PART	Poor	Poor	Partly disintegrated	Fully disintegrated
BOTTOM PART	Good	Good	Good	Good

3. MOISTURE HOLDING CAPACITY

It is interesting to note that neither rate of moisture absorption nor the depth of moisture penetration is correlated with critical humidity. Where neither the depth of moisture correlate with rate of moisture absorption, is a result of differences in "Moisture holding capacity."

Moisture holding capacity of various fertilizers was calculated as milligrams of moisture per cubic centimeter of fertilizer by dividing the moisture absorption per square centimeter by the depth of penetration in centimeter.

$$\text{MHC mg/cm}^3 = \frac{\text{MA}}{\text{MP}}$$

The above values were also converted to percent moisture holding capacity by weight per unit volume (bulk densities) of the fertilizers in the cup, as under

$$\%MHC = \frac{MHC\ mg/cm^3}{(OW / V) \times 1000} \times 100$$

where MHC % = Moisture holding capacity %
MHC mg/cm^3 = Moisture holding capacity mg/cm^3
OW = Original weight of sample gm.
V = Sample cup volume cm^3.

The holding capacities thus calculated, represent the maximum amount of moisture that a granule will absorb before it becomes so wet that moisture will be transferred to adjacent granules by capillary adhesion and action. High moisture holding capacity is a desirable characteristics, that can offset the effect of high rate of moisture absorption. The experiment detail is shown in Table 3 at 80 /90 % RH with 0.05 / 0.1 % coating. The experiment was run for 96 hours. Where MHC low values were observed with 0.1 % coating at 90 % RH. While in CAN, no value of moisture penetration is observed, hence values of MHC could not be calculated.

Table 3 : Moisture holding capacity (in mg/cm^3)

ANP PRODUCT		**0.05% ACA Coating**			**0.01% ACA Coating**		
	Uncoated	**A**	**B**	**C**	**A**	**B**	**C**
AT 80% RH	107.9	122.1	118.3	140.9	122.3	129.0	148.0
AT 90% RH	152.2	125.9	134.0	155.9	120.1	121.3	115.8

Sample A and B are liquid and sample C is semisolid anticaking agents

4. CAKING TENDENCY

Hygroscopicity caused by humidity results in wetting and caking of ANP fertilizer with prolonged exposure and penetration of top surfaces moisture into fertilizers bed, become quite deep. Also conveying or handling the fertilizers in a humid atmosphere prior to bagging or pile building can introduce moisture that later will prompt caking. Under the hygroscopic studies at 80 / 90 % RH, the ANP fertilizer developed caking in three forms (1).Top surface became watery with disturbance in granule geometry (2). Immediate after watery surface, 2nd layer of caking observed in all samples which remained hard in uncoated samples and soft in coated samples (3). Just after 2nd layer up to bottom, liquid coated products (ANP/ CAN) were found free flow, the semi viscous product coating contributed channeling across granule bed up to bottom of jar and caking observed. The channel had not only reduced the free flow ability of granules, but also changed the granules geometry and under high humid conditions, it led to the physical separation of chemical constituents of mixed fertilizer, like separation of ammonium nitrate in ANP, which is highly undesirable. Due to this deficiency (channeling and physical separation of chemical constituents under humid conditions) in semi viscous product the application of liquid anticacking agent is found more desirable. The percentage caking observed of total sample weight is shown in Table 4 at 80 /90 % RH with 0.05 / 0.1 % coating. The experiment was run for 96 hours.

Table 4 : % Caking observed after experiment

PRODUCT		0.05% ACA Coating			0.01% ACA Coating		
	Uncoated	**A**	**B**	**C**	**A**	**B**	**C**
AT 80% RH (ANP)	8.1	5.6	5.0	6.6	4.6	4.9	5.2
AT 80% RH (CAN)	7.3	5.5	5.9	6.7	3.9	3.5	4.2
AT 90% RH (ANP)	14.9	12.3	11.8	13.3	9.1	9.5	11.7
AT 90% RH (CAN)	7.4	5.2	4.0	6.7	3.3	2.8	4.9

Sample A and B are liquid and sample C is semisolid anticaking agents

EVALUATION OF EFFECTIVENESS OF ANTICAKING AGENTS

(A) Reduction in Hygroscopicity of Fertilizers

Various mechanisms have been proposed for the effectiveness of anticaking agents like protection from moisture, spreading of liquid film modification of crystal make up/behavior, inhibition of dissolution and crystallisation and modification of bond tensile strength, on their application to fertilizers like ANP, CAN.

The effectiveness of anticaking agents application is observed by the data generation of reduction in hygroscopicity for coated ANP, CAN products at 80/90 % RH, with 0.05/0.1 % coating of different Anti caking agents with respect to Uncoated ANP, CAN, as shown in Figures 11 and 12 and Table 5.

Table 5 : % Reduction in hygroscopicity

		0.05% ACA Coating			0.01% ACA Coating		
	Uncoated	**A**	**B**	**C**	**A**	**B**	**C**
ANP PROD (80% RH)	-	9.5	14.5	8.3	10.2	14.8	8.9
ANP PROD (90% RH)	-	15.7	18.4	14.1	24.3	25.3	22.9
CAN PROD (80% RH)	-	11.2	12.1	7.7	13.7	19.1	12.5
CAN PROD (90%RH)	-	16.3	14.4	11.9	23.3	20.1	18.2

Sample A and B are liquid and sample C is semisolid anticaking agents

(B) Evaluation of the effectiveness of anticaking agent is further confirm by application of only one liquid antiquating agent at 0.05 % and 0.10 % dose level on ANP and the moisture absorption was closely monitored on daily / cumulative basis at 90 % RH as shown in Figures 13 and 14 and Tables 6 and 7. This shows that % moisture absorption is reduced by 16. 1 % at 0.05 % coating and 25.3 at 0.1 % coating of anticaking agent with respect to uncoated product.

Table 6 : Daily moisture absorption (mg / cm2) at 90 % RH of uncoated and coated product at different dose level.

Sample	0 - 24 Hrs.	24 - 48 Hrs.	48 - 72 Hrs.	72 - 96 Hrs.
Uncoated	132.1	108.0	86.0	63.5
0.05 % Coating	103.1	89.2	77.9	56.5
0.10 % Coating	88.8	78.9	68.3	54.9

Table 7 : Cumulative moisture absorption (mg / cm2) at 90 % RH of uncoated and coated product at different dose level.

Sample	24 Hrs.	48 Hrs.	72 Hrs.	96 Hrs.
Uncoated	132.1	240.0	326.1	389.5
0.05 % Coating	103.1	192.3	270.1	326.6
0.10 % Coating	88.8	167.7	236.0	290.9

Therefore, reduction in daily / cumulative moisture absorption by coated ANP product with respect to uncoated product confirm the suitability of anticaking agent application on hygroscopic fertilizers like ANP / CAN. The dose level is optimised on cost / benefit ratio by maintaining the quality requirement of fertilizer.

Though the % efficiency in the reduction on crushing load of fertilizer is observed > 50 % at 0.05% coating level in all the anticaking agents, but their effectiveness against hygroscopicity was found varying from 8.3 % to 25.3 % in total.

CONCLUSION

To minimise the hygroscopic behavior of ANP/CAN fertilizers and to ascertain and maintain its satisfactory physical properties like good drillability, flowability, absence of caking and resistance to humidity, various measures have been taken at GNFC, such as :

1. PRODUCT MOISTURE

The moisture of the product is kept as low as possible, (desirable <0.6 % by weight) as product with high moisture tends to absorb more water then a product with low moisture.

2. PRODUCT COOLING

Low temperature of the product at the time of bagging/storage.i.e.<35-40°C.

3. PROPER GRANULATION AND SCREENING

Large particles with reduced surface area is desirable to absorb low moisture.

4. CONTROL OF STORAGE CONDITION AND PACKING

The ANP/CAN products are packed in heat sealed double liner and moisture resistant bags, to minimise the effect of outside atmosphere humidity on the product.

5. INTERNAL CONDITIONERS

Fertilizer product like MAP/DAP and ANP made from wet process of phosphoric acid, characteristically contain significant quantities of iron and aluminum phosphate impurities. These impurities serve as effective internal conditioners in these products. The iron and aluminum phosphates are found in the product (ANP granules) as "Amorphous - Gels", that harden the ANP granules and there by increase the crushing strength and reduce the porosity of the product. Similarly in processing of CAN products, conc. H_2SO_4 is added in pure ammonium nitrates(92 - 96 %), to maintain sulphate content 0.25 to 0.40 %. This ammonium nitrate is mixed with $CaCO_3$, where SO_4^{-2} ions work as binding agent and give good crushing strength to CAN product, along with minimisation of abrasion.

6. APPLICATION OF ANTICAKING AGENTS

The anticaking agents work in hydrophobic form on wetting which makes the surface of the granule resistant to water, so that rate of moisture absorption by the granules is reduced, as well as a hydrophobic barrier between two granules is provided to prevent bonding due to capillary adhesion, and therefore restrict caking under the influence of humid conditions and intact granule geometry of the product and make them free flowing, which become handy during drilling.

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MOISTURE ABSORPTION in mg / cm2 AT 80% RH COATING WITH 0.05 % ACAS ON **ANP**

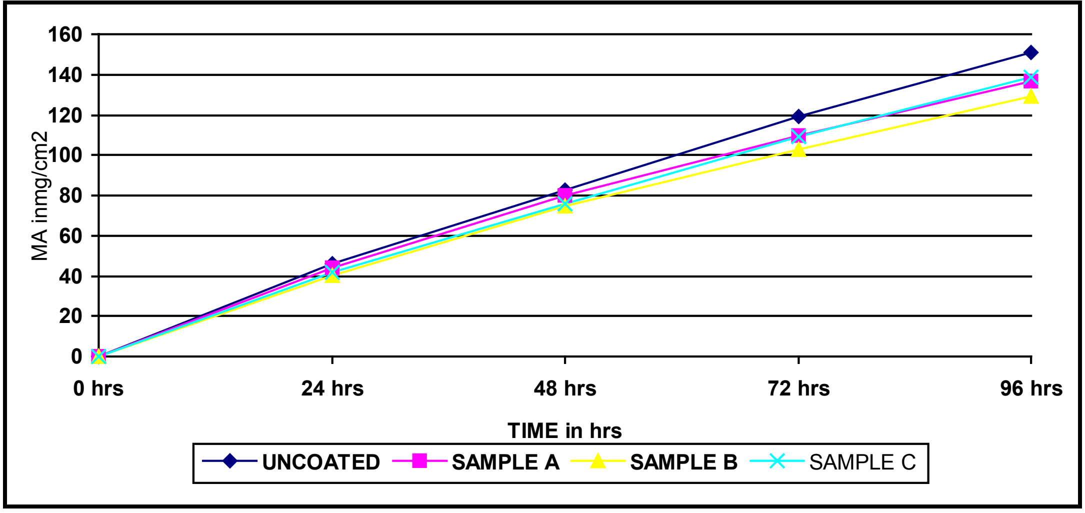

FIG - 3

MOISTURE ABSORPTION in mg / cm2 AT 80% RH COATING WITH 0.10 % ACAS ON ANP

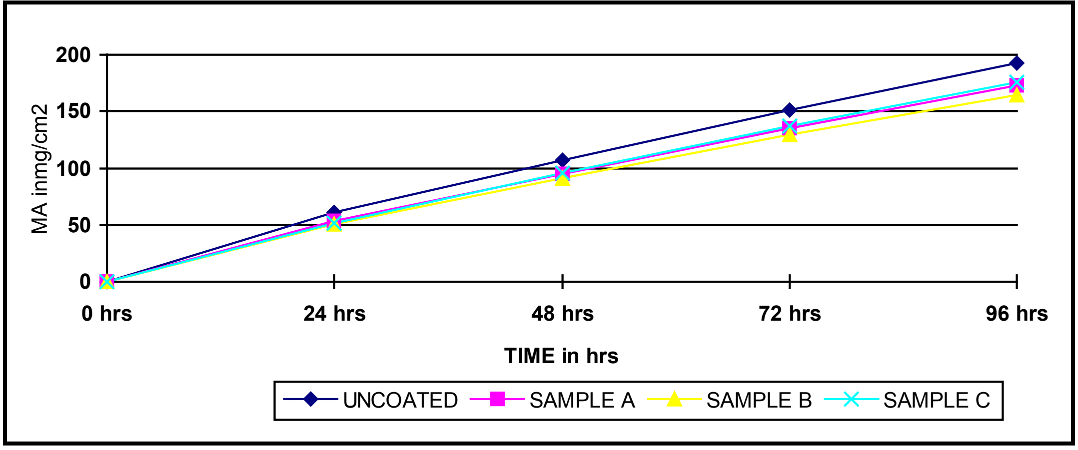

FIG - 4

MOISTURE ABSORPTION in mg / cm2 AT 80% RH COATING WITH 0.05 % ACAS ON **CAN**

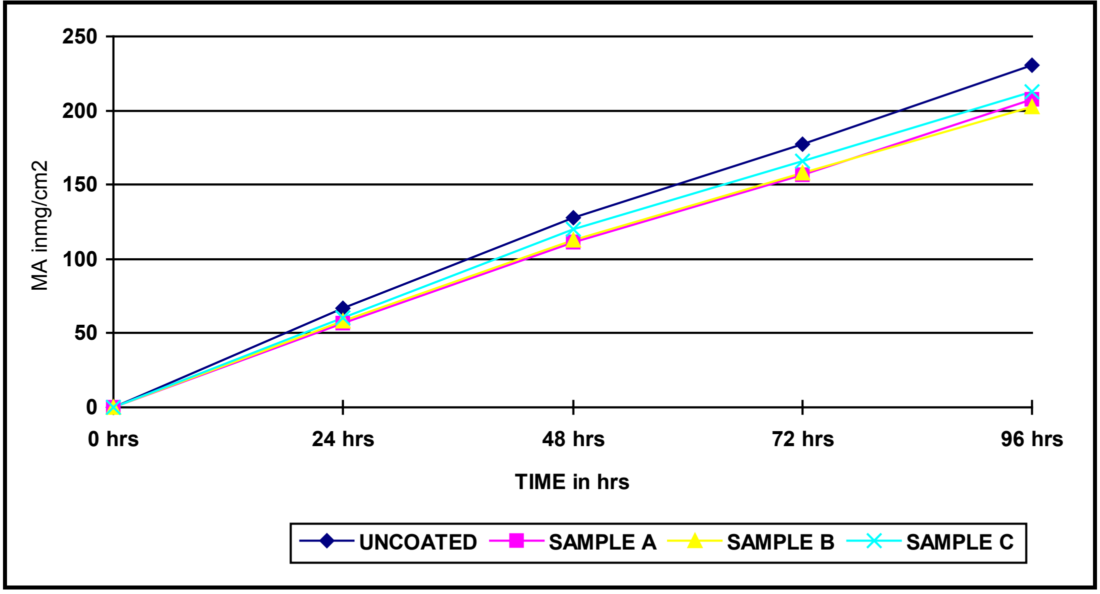

FIG - 5

MOISTURE ABSORPTION in mg / cm2 AT 80% RH COATING WITH 0.10 % ACAS ON **CAN**

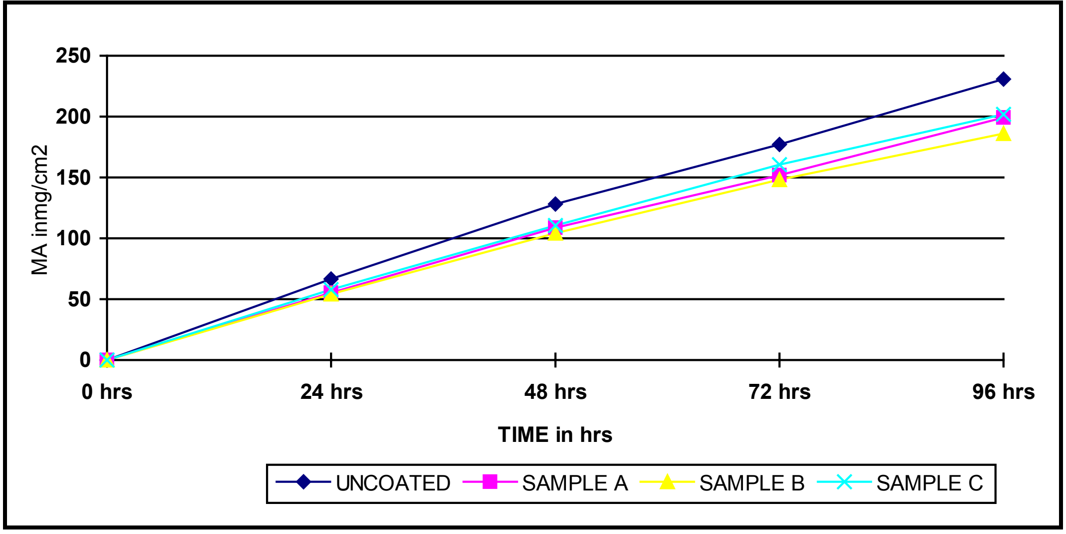

FIG -6

MOISTURE ABSORPTION in mg / cm2 AT90% RH COATING WITH 0.05 % ACAS ON **ANP**

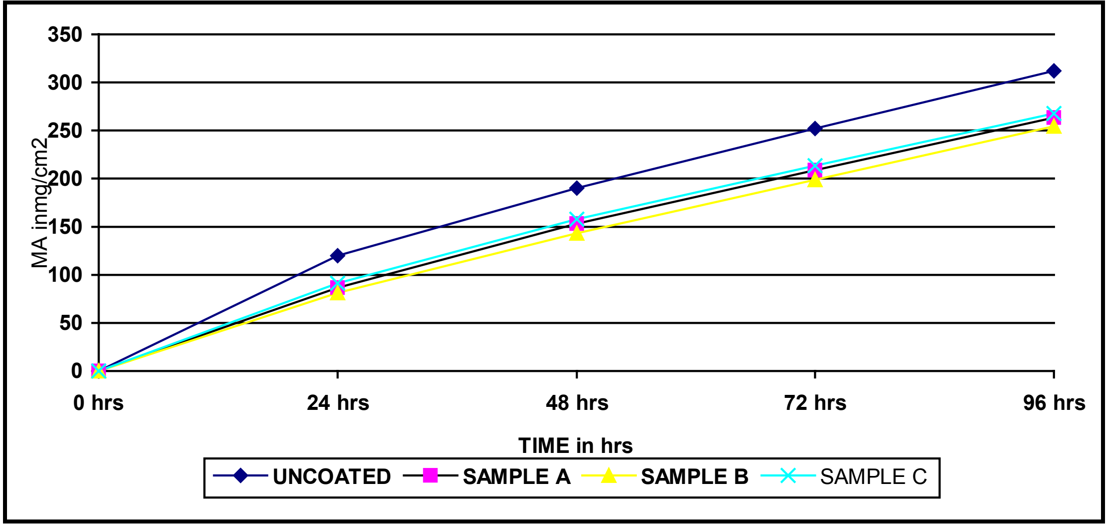

FIG - 7

MOISTURE ABSORPTION in mg / cm2 AT 90% RH COATING WITH 0.10 % ACAS ON **ANP**

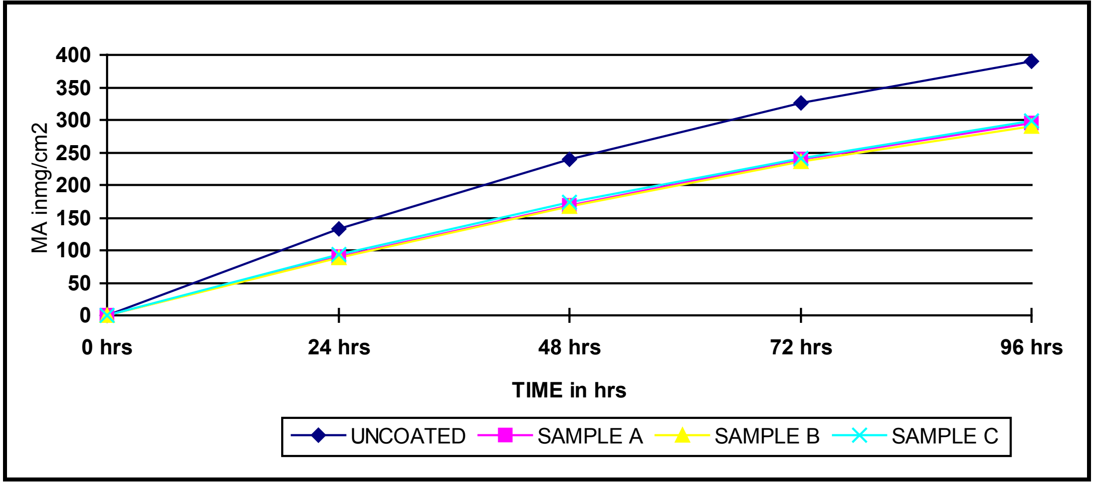

FIG - 8

MOISTURE ABSORPTION in mg / cm2 AT 90% RH COATING WITH 0.05 % ACAS ON **CAN**

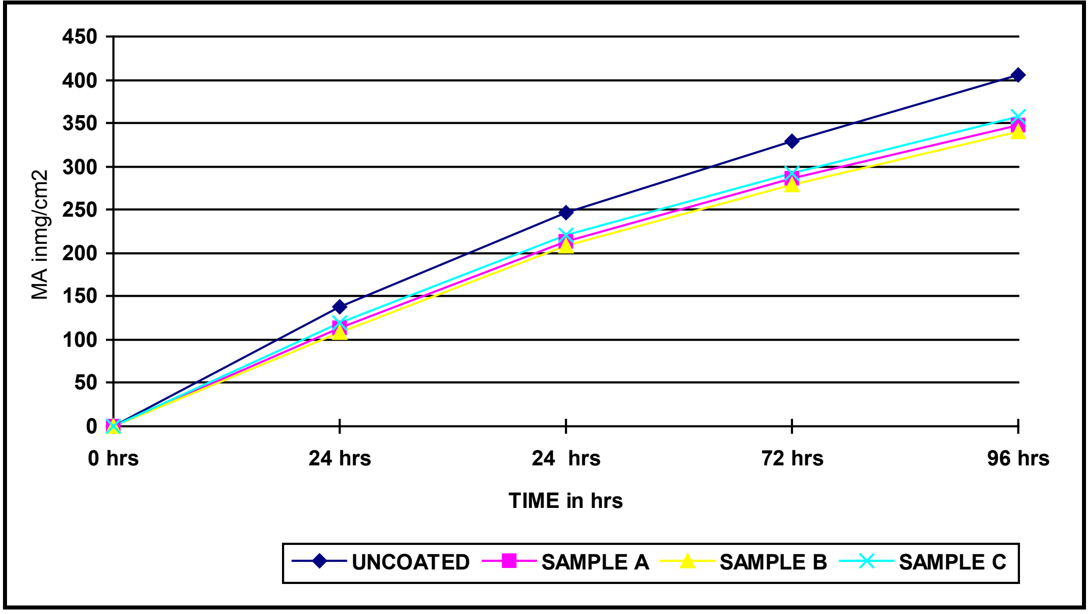

FIG - 9

MOISTURE ABSORPTION in mg / cm2 AT 90% RH COATING WITH 0.10 % ACAS ON **CAN**

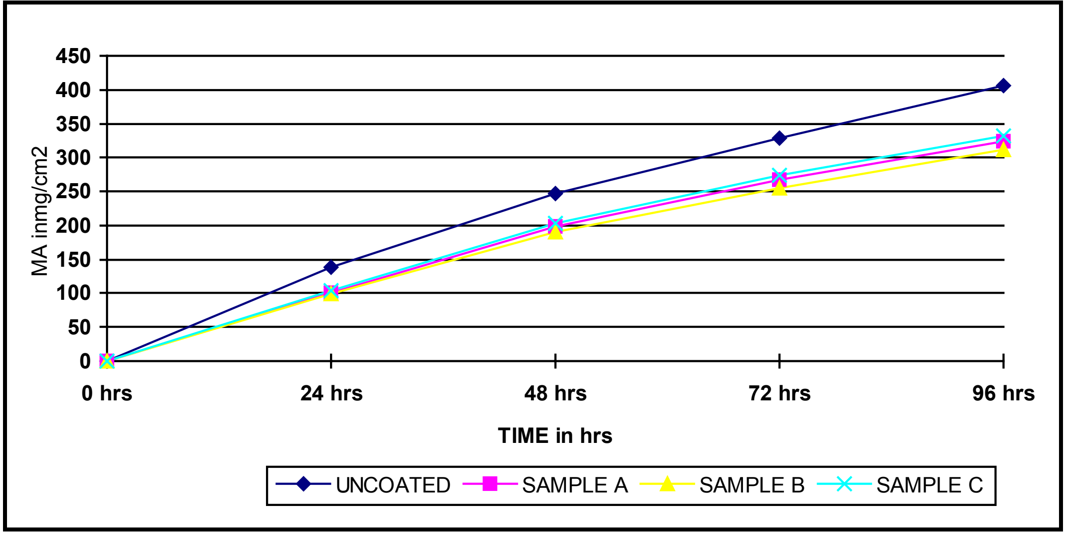

FIG -10

REDUCTION IN HYGROSCOPICITY AT 80% RH WITH DIFF.DOSE.LEVELS ACAS ON ANP /CAN

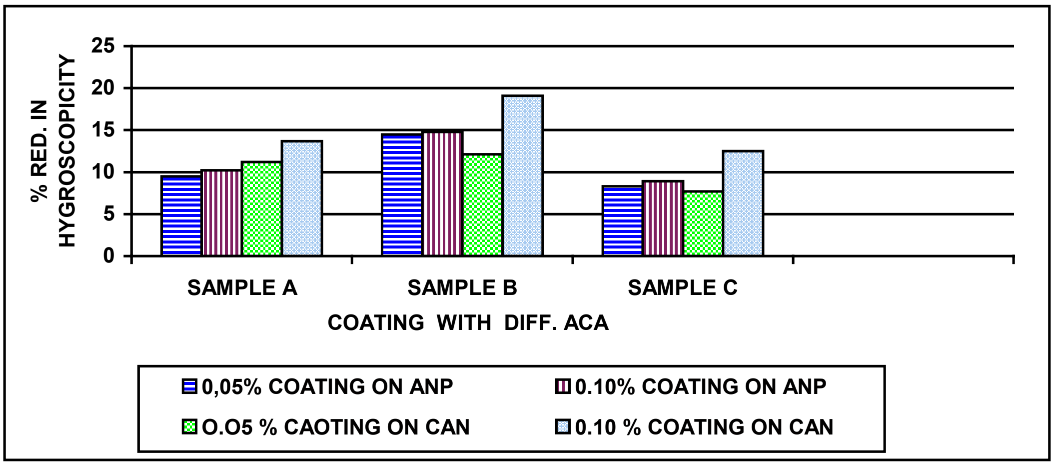

FIG -11

REDUCTION IN HYGROSCOPICITY AT 90% RH WITH DIFF.DOSE.LEVELS ACAS ON ANP /CAN

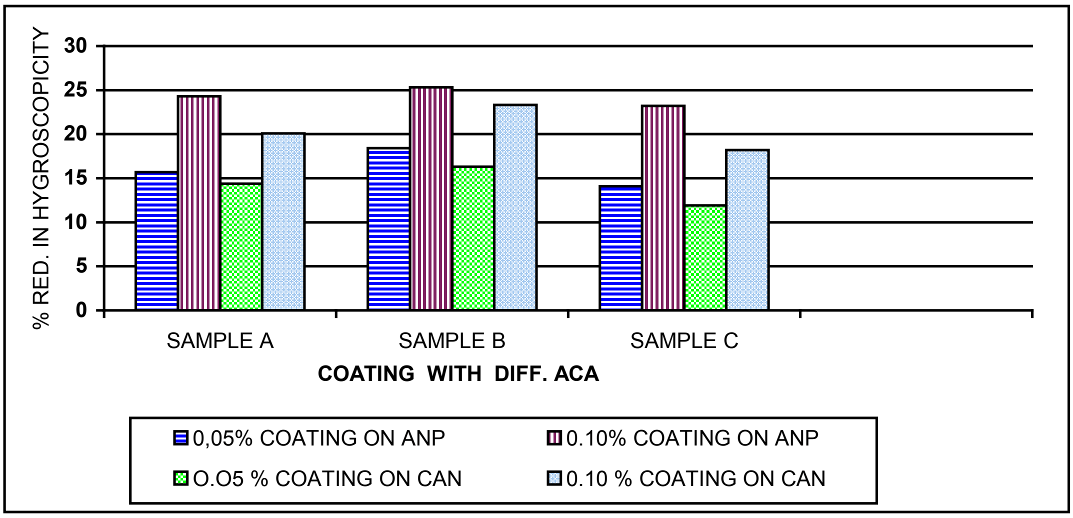

FIG -12

MOISTURE ABSORPTION AT 90% RH COATING WITH DIFF DOSE LEVEL OF ACA ON **ANP**

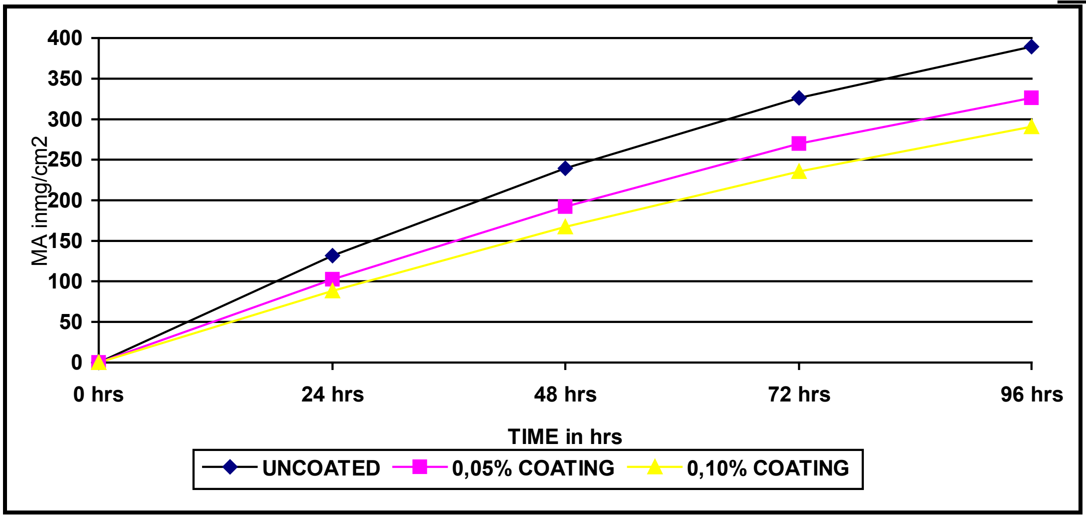

FIG - 13

DAILY MOISTURE ABSORPTION at 90% RH COATING WITH DIFF.DOSE LEVEL OF ACA on **ANP**

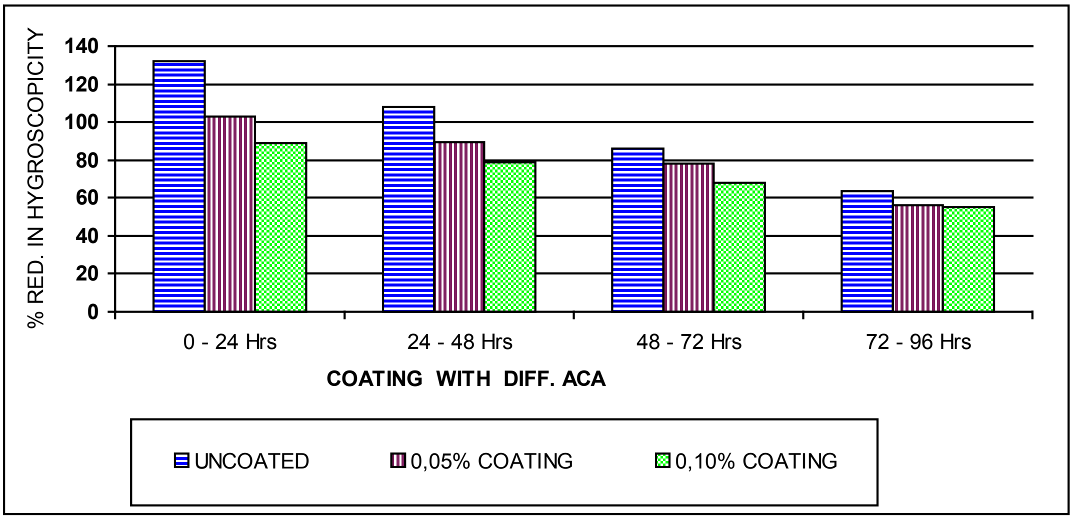

FIG - 14

HUMIDITY CONTROLLER CIRCUIT

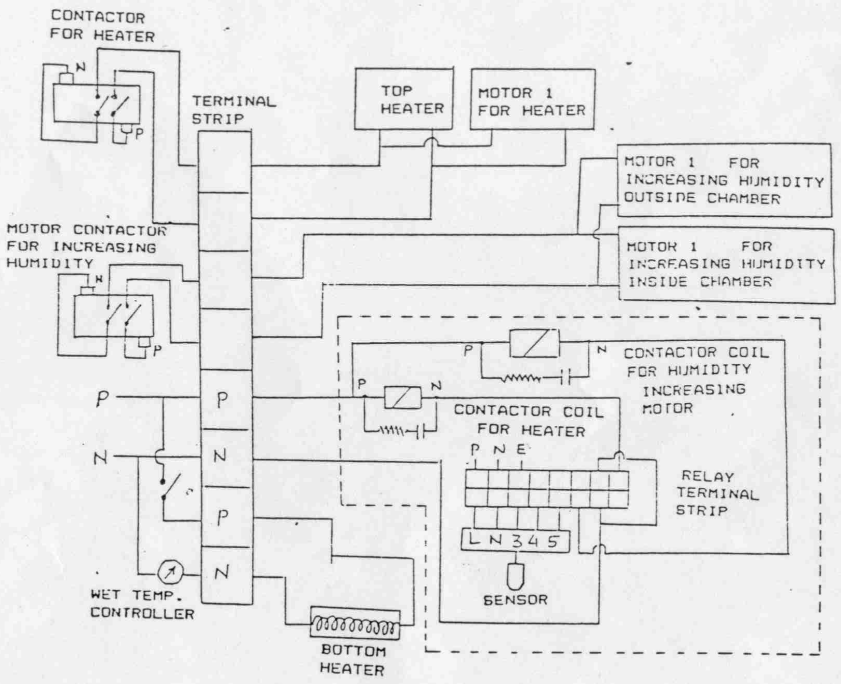

FIG-1

GLASS CYLINDER

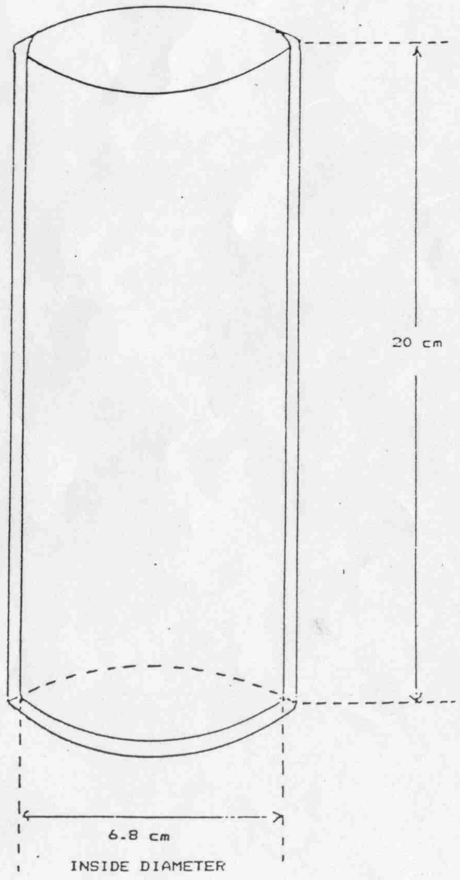

FIG - 2