

## Effect of Humidity on Physico-chemical Properties of Hydrus Aluminum Oxide

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**Abstract**—The effect of humidity on the aging process of hydrus aluminum oxide prepared by the reaction of aluminum chloride and sodium bicarbonate solution at pH 7.8, which was then kept in various atmosphere under relative humidity at 37° was observed by the measurements of acid consuming capacity, X-ray diffraction and IR absorption.

The humidity was one of the important factors influencing the aging process of hydrus aluminum oxide during storage. The higher the humidity, the more was accelerated age, crystalize and loss in acid reactivity. Depending on the humidity, the aging product was different, especially, in the case of up to the relative humidity of 72%, it forming bayerite. On the other hand, the hydrus aluminum oxide aged below the relative humidity of 50% was still amorphous even after 120 days storage. When hydrus aluminum oxide was aged under higher humidity, definite IR absorption bands develop as the hydroxys become part of an ordered structure, and it showed their characteristic absorption band around 1630 and 1060  $\text{cm}^{-1}$ .

Hydrus aluminum oxide is an effective antacid, although many aspects of its structure and acid reactivity are not fully understood. Many studies have been made on the excellent properties of hydrus aluminum oxide as a gastric antacid as well as on the diverse physico-chemical behaviors. Especially, a validity of hydrus aluminum oxide as medicinal preparations is influenced by the antacidic reactivity<sup>1)</sup>.

One of the important factors which may control the antacidic reactivity is considered to be a crystal form and especially it is necessary to be amorphous. Many reports<sup>2-14)</sup> have been found on this facts as well as on the manufacturing methods and the crystal transformation<sup>15-25)</sup>. As to the aging phenomenon, Funaki<sup>2)</sup>, Santos *et al.*,<sup>5)</sup> Moscou and Vlies<sup>10)</sup>, Marboe and Bentur<sup>26)</sup>, and Yamaguchi<sup>27)</sup>, studied and presented concurrent conclusions that, though a slight difference may be observed depending on the aging conditions, bayerite-like crystalline body was once produced and examined by X-ray crystallographical methods.

Generally, the aging of hydrus aluminum oxide is influenced by the surrounding atmosphere and many studies have been reported on this matter. The crystallization on aging proceeds very rapidly under the condition of a higher pH and on this fact many investigations have been carried out as one of the important factors in manufacturing process. Marboe and Bentur<sup>25)</sup> examined the suitable pH range for obtaining the amorphous substance by the reaction between aluminum salts and aqueous ammonia. With aging, structural rearrangement occurs to form more thermodynamically stable system<sup>11,21)</sup> a polymerization-like process may produce a highly ordered system resistant to attack by acid<sup>28-31)</sup>.

The aging process of commercial hydrus aluminum oxide on keep-standing under various relative humidities or in water was investigated by Nogami *et al.*,<sup>32)</sup> that the final products on aging would be supposed to be a mixture of bayerite and gibbsite. Nail *et al.*,<sup>34)</sup> reported that IR analysis offers additional advantages over X-ray diffraction in terms of lower cost of instrumentation and more universal access to IR spectrophotometers, it is suitable for routine monitory of hydrus aluminum oxide.

The purpose of this study was attempted to observe the effect of humidity on the aging processes of hydrus aluminum oxide, which was kept in various atmosphere under relative humidity at 37° by the measurements of acid consuming capacity, X-ray diffraction and infrared absorption spectra.

## EXPERIMENTAL

**Materials**—All chemicals used were either official or reagent grade.

**Table I**—Conditions for obtaining the adsorption isotherm of water on hydrus aluminum oxide

Sample No.	Salt and acid used	Relative humidity at 30° a)
1	K <sub>2</sub> SO <sub>4</sub>	96
2	NaNO <sub>3</sub>	72
3	44%~H <sub>2</sub> SO <sub>4</sub>	50
4	99.5%~H <sub>2</sub> SO <sub>4</sub>	0

a) International critical Table, 3, 291 (1928)

### Preparation of hydrus aluminum oxide

—Hydrus aluminum oxide was prepared by the reaction of aluminum chloride and sodium bicarbonate solution at pH 7.8<sup>35)</sup>.

**Controlling humidity**—Saturated inorganic salt solutions and various concentrations of sulfuric acid were used for maintaining constant humidities as described in Table I. The solutions were poured in the small desiccators, then placed in the constant temperature incubator at 37°±2. The hydrus aluminum oxide in petri-dish was kept in the

desiccator for moistening and aging.

**Analytical procedures**—The acid consuming capacity test was modified by titrating to pH 3.5 rather than using bromophenol blue TS, as given in the Korean Pharmacopeia. The antacid property of the hydrous aluminum oxide is given as a percentage of the theoretical acid-consuming capacity.

For X-ray analysis, a sample of the hydrous aluminum oxide was air dried at 37° and ground to a fine powder with an agate mortar and pestle. The diffraction pattern was recorded from 5 to 60° of  $2\theta$  under the following conditions: Cu  $K_{\alpha}$  radiation, 40 Kv, 20 mamp, 500 cps full scale, and 2°/min. scan. speed using Shimatzu-GX-2B X-ray diffractometer.

IR spectra of hydrous aluminum oxide were obtained by KBr disk using Jasco-IR-S IR spectrophotometer. The spectra were recorded from 4000 to 700  $\text{cm}^{-1}$  with normal scan speed.

## RESULTS AND DISCUSSION

A plot of the logarithm of the acid consuming capacity of the hydrous aluminum oxide *versus* time at 37° is shown in Fig. 1. The loss in acid reactivity follows apparent first-order kinetics. The slopes are  $-1.48 \times 10^{-3}$ (1),  $-1.65 \times 10^{-3}$ (2),  $-1.90 \times 10^{-3}$ (3) and  $-2.26 \times 10^{-3}$ (4)  $\text{day}^{-1}$ , respectively and y-intercepts are 89.8% (1), 89.7% (2), 87.2% (3) and 84.9%

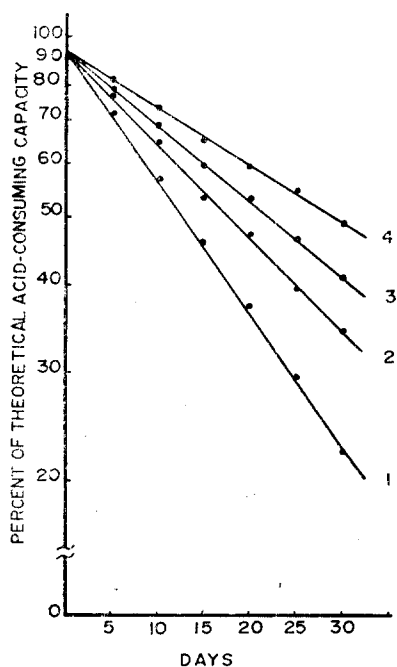


Fig. 1—Change in acid-consuming capacity of hydrous aluminum oxide during aging at 37° in various conditions of relative humidity. Key: 1.0 %; 2.50%; 3.72%; 4.96%

(4) each by linear regression analysis and the linear correlation coefficients are  $-0.989$  (1),  $-0.987$ (2),  $-0.980$ (3) and  $-0.976$ (4), respectively. This shows the negative correlation between time and acid-consuming capacity.

As the structure of hydrous aluminum oxide is unknown, it is difficult to clarify the reason of the dependence of aging rate on the degree of humidity. However it may be related to the aging of hydrous aluminum oxide and the formation of bayerite would be accelerated by the addition of alkali so as to remove protons easily<sup>26</sup>). That is,  $\text{NH}_3$  molecule may transform to  $\text{NH}_4$  ion and protons on hydrous aluminum oxide may tend to be decreased, therefore, it is considered that the average protonic density of  $\text{Al}^{3+}$  ionic groups, surrounded by hydration shell, could be changed. Hence, if the degree of humidity as well as the concentration of hydrogen ion is high, such an action would naturally be strengthened,

then the aging rate would be fastened.

Depending on the difference of humidity, the surface of hydrous aluminum oxide undergoes different influence and domain having different properties in consideration to be produced. Therefore, it is expected that the crystallization of growing domain may afford different kinds of crystalline substance.

The X-ray diffraction analysis showed a clear differences between the samples in Fig. 2. Both sample No. 3 and sample No. 4 which showed almost no neutralizing reactivity any more after 30 days keep-standing under the humidity, 76% and 96%, had been in crystallization. On the other hand, both sample No. 1 and sample No. 2 showed to be amorphous when they were aged for 120 days under the humidity, 0% and 50%. But X-ray diffraction appears to be relatively insensitive to the structural changes occurring during aging that result in a diminished acid reactivity. Sample No. 3 and sample No. 4 showed the diffraction of hydrous aluminum oxide crystals, the characteristic difference was around  $18^\circ$  as  $2\theta$  value by Cu  $K_\alpha$  radiation, and this portion was found by Nogami *et al.*<sup>16,32,33)</sup> that the tips of the peak were clearly separated into two peaks, being  $18.8^\circ$  ( $d=4.72 \text{ \AA}$ ) and  $18.4^\circ$  ( $d=4.82 \text{ \AA}$ ). The former value corresponded to bayerite and the latter to gibbsite, but the sample No. 3 and No. 4 aged under above 72% relative humidity are considered to be a bayerite. These results are different from Nogami *et al.*'s<sup>32)</sup> and Fujie *et al.*'s<sup>34)</sup> conclusions. A different fact was that the crystallization process by aging was not observed in two steps X-ray crystallographically. In Fig. 3, the aging process in various relative humidity was recorded with the laps of time. At the beginning of aging, a change was observed around  $36\sim 42^\circ$  of  $2\theta$  value and it is inclined to increase gradually. Next after a certain period of time, a change was observed in a portion of  $18\sim 20^\circ$  of  $2\theta$  which developed rapidly to the strongest peak with the laps of time as shown in Fig. 3. This phenomenon is supposed to have some relation to the change of neutralizing rate<sup>32)</sup> which was increased a certain period of time after the beginning of aging.  $36\sim 42^\circ$  of  $2\theta$  value being  $2.1\sim 2.5 \text{ \AA}$  of interplanar distance, the phenomenon observed at an early stage of aging prior to the appearance of peak at  $18\sim 20^\circ$  of  $2\theta$  was explained that a pair of atoms having  $2.1\sim 2.5 \text{ \AA}$  atomic distance was arranged orderly, which was considered to be in reactive state with acid. Furthermore, an appearance of the peak at  $18\sim 20^\circ$  of  $2\theta$  indicated that a real crystallization was proceeded and so the atoms were to be arranged in inreactive state with acid.

The IR spectrum shown in Fig. 5 is typical patterns of a freshly prepared hydrous aluminum oxide. The broad diffuse peak centered at about  $3400\sim 3500 \text{ cm}^{-1}$  corresponds to  $\nu\text{O-H}$  structural hydroxy and absorbed water. The band at  $1630 \text{ cm}^{-1}$  is  $\delta\text{O-H}$  of absorbed water. The broad peak at about  $1060 \text{ cm}^{-1}$  represents an O-H deformation vibration. Hydrous aluminum oxides containing carbonate have a peak at the  $1440 \text{ cm}^{-1}$  region as well as at  $1550 \text{ cm}^{-1}$ <sup>135)</sup>.

The  $\nu\text{O-H}$  and  $\delta\text{O-H}$  are markedly affected by their chemical environment, since the broad absorption band in the  $3200\sim 3600 \text{ cm}^{-1}$  region of the IR spectrum of the fresh one indicates

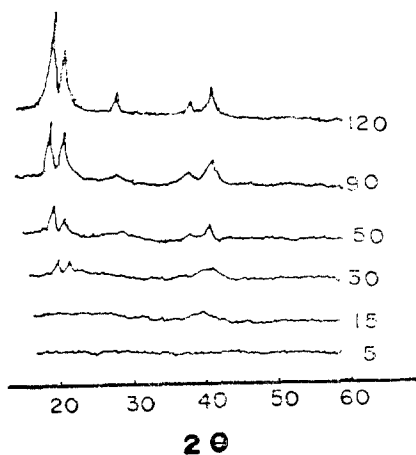


Fig. 2—X-ray powder diffraction pattern of hydrous aluminum oxide aged under below 50% R.H.

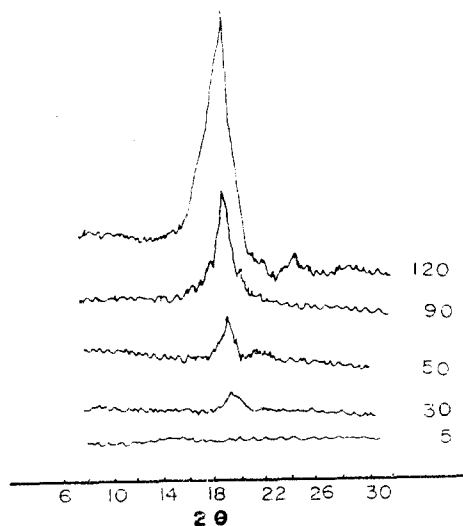


Fig. 3—Change in X-ray diffraction pattern of hydrous aluminum oxide during aging under 96% R.H. at 37°.

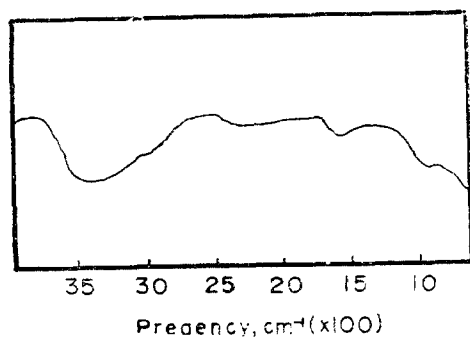


Fig. 4—X-ray diffraction pattern of hydrous aluminum oxide aged under 96% R.H. for 120 days by  $\text{Cu-K}\alpha$  radiation at a scanning speed of  $1/2^\circ$  per min.

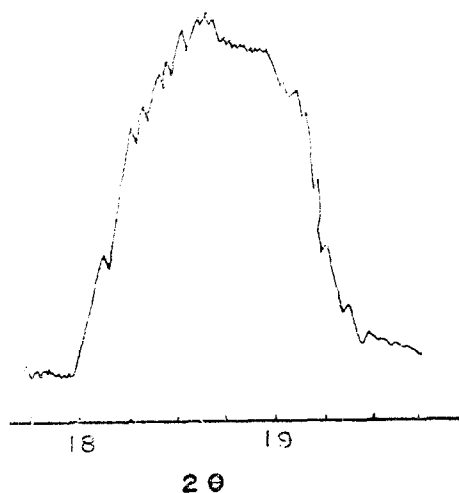


Fig. 5—IR spectrum of freshly prepared hydrous aluminum oxide.

O-H groups in many environments, thus indicating the highly disordered nature of the fresh hydrous aluminum oxide<sup>37</sup>.

The IR spectrum of the sample showed in Fig. 6. 7. much resemblance in absorption, though there are some differences in intensity. The big broad absorption band around 3400

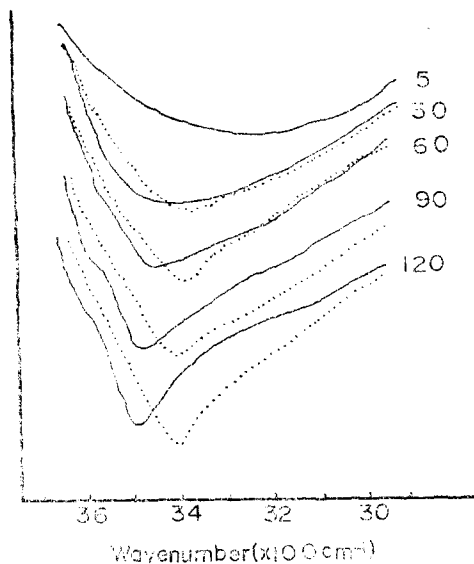


Fig. 6—Change in O-H region of IR spectrum of hydrous aluminum oxide during aging at 37°. Key: solid line, 96%; dotted line, below 50%.

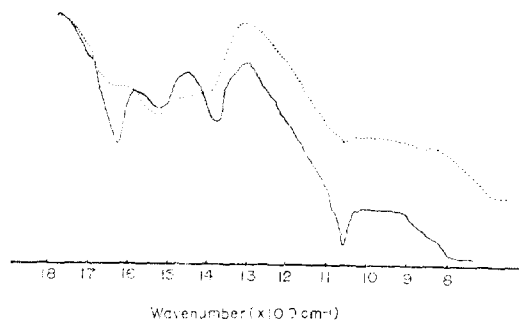


Fig. 7—Change in O-H region of IR spectrum of hydrous aluminum oxide during aging at 37° for 120 days, respectively. Key: solid line, 0% R.H.; dotted line, 96% R.H.

$\text{cm}^{-1}$  and the two step broad absorption around  $1630 \text{ cm}^{-1}$  and  $1060 \text{ cm}^{-1}$  with weak extent of intensity, was recognized specific.

The  $\nu\text{O-H}$  region of the IR spectrum is shown for various aging periods in Fig. 6. The sample aged for 15 days has an IR absorbance pattern characteristic of a highly disordered structure. As the sample ages, the  $\nu\text{O-H}$  region of higher humidity occurs toward high frequency region than that of the lower humidity.

The spectral changes in the O-H deformation region are shown in Fig. 6. As the sample ages, a shoulder develops at  $1060 \text{ cm}^{-1}$  and eventually becomes a well-resolved peak.

The absorption around  $1000 \text{ cm}^{-1}$  or lower frequency has been similarly observed with metal complexes in which water is co-ordinated<sup>40)</sup>. The absorption around  $1400 \text{ cm}^{-1}$  is usually assigned to be attributed to carbonate, and it is better to interpret that the absorption around  $1400 \text{ cm}^{-1}$  is considered to be a overtone of recognizable around  $700 \text{ cm}^{-1}$ <sup>39)</sup>. However, both sample No. 3 and sample No. 4 showed such a clear difference with the laps of time that the absorption band of  $\nu\text{O-H}$  around  $3500\sim 3400 \text{ cm}^{-1}$  became narrower in its width to appear as a sharp band around  $3500 \text{ cm}^{-1}$ . The absorption band shifted toward higher frequency owing to the process of aging, indicating that the hydrogen bond in the structure of hydrous aluminum oxide decreased depending on the aging. Since the decrease of hydrogen bond in the structure could be assumed from the change of infrared spectra, at the beginning in the transfer process of the disordered atoms or atomic group to the orderly arrangement for a certain crystal structure, structural portions of atom or atomic pair to increase the basicity of solid were supposed to increase temporarily in the surface to accelerate the

neutralizing rate<sup>41-42</sup>). Furthermore, as the aging proceeded, and also an orientation of molecular structure would be restrained to ward uniformity, it was supposed that the neutralizing reactivity would be lost when finally crystallization was completed. The reason of these differences of aging under various humidity was also considered to be caused perhaps by the difference of chemical and surface structure depending on the difference of storing humidity. According to the degree of humidity, hydrous aluminum oxide also have different aging properties.

Usually crystallization was considered to be proceeded in two separate steps, that is, the nucleation and growth<sup>43-46</sup>). The appearance of the peak at  $18\sim 20^\circ$  of  $2\theta$  and its development, as described above, were considered to corresponded the growth period on crystallization, and the fact that at an early stage of aging, a very broad and weak diffraction appeared at around  $36\sim 42^\circ$  of  $2\theta$  was interpreted to be the induction period. The induction period of crystallization was shortened as the degree of humidity became higher, but it was difficult to find an accurate relationship between rate and degree. However, in the case of relative humidity of below 50%, the crystallization was supposed to proceed further after 120 days and was almost completed by the aging for 30 days in the cases of up to 72% relative humidity.

On the aging under humidity, similar changes in the cases of aqueous ammonia were recognized at the same positions. But, though the positions of absorption were the same, still differences were observed. Especially, the absorption around  $3500\text{ cm}^{-1}$  was sharp and simple compared with that of the sample aged in aqueous ammonia<sup>33</sup>), which showed in separated peaks. This tendency was especially remarkable when the degree of humidity was high. This phenomenon was given to the state of water molecules surrounding  $\text{Al}^{3+}$  ion in the structure of hydrous aluminum oxide and the hydrogen bond was remarkably decreased.

From these results, it seems possible that, as the aging proceeds, the structure of hydrous aluminum oxide, in which aluminum ion is bound with such water molecules as are rich in hydrogen bond tends to change to the orderly arrangement of  $\text{Al-OH}$  and water coordinated to aluminum. And the hydrous aluminum oxide need to be kept in atmosphere as dry as possible to prolong its reactivity.

## CONCLUSION

1. The humidity was one of the important factors influencing the aging process of hydrous aluminum oxide during storage. The higher the humidity, the more was accelerated age, crystallize and loss in acid reactivity.

2. Depending on the humidity, the aging product was different, especially, in the case of up to the relative humidity of 72%, it forming bayerite. On the other hand, the hydrous aluminum oxide aged below the relative humidity of 50% was still amorphous even after 120 days storage.

3. As hydrous aluminum oxide was aged under higher humidity, definite IR absorption

bands develop as the hydroxys become part of an ordered structure, the aged hydrated aluminum oxide in higher humidity showed their characteristic absorption band around 1630 and 1060  $\text{cm}^{-1}$ .

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