Abstract—A new adsorbent for ammonia was developed by chemical treatments of active carbon. From adsorption isotherm observations at 25°C, it was shown that active carbon, which intrinsically little adsorbs ammonia, was improved to adsorb ammonia to various extents up to 8.40 mmol/g at Langmuir's monolayer coverage by oxidation with nitric acid solution and was further promoted by the impregnation of metals such as Ni, Co and Cu. The other adsorbents such as silica gel, alumina gel and aluminum oxide hydroxide were comparatively studied. Metal impregnation promoted the adsorptivities of these adsorbents for ammonia as well. Among the tested adsorbents, nickel impregnated oxidized active carbon showed the greatest adsorptivity of 9.4 mmol/g.

The copper impregnated oxidized active carbon was packed in gas mask canisters and tested for air stream containing ammonia, proving that it serves for longer period than the adsorbents in current use.

The removal of ammonia from the environmental air is often the needs in industrial and public hygiene and industrial processes. There are some kinds of adsorbents currently used for ammonia which include cupramite, aluminum oxide hydroxides, silica gel and sulfonated coal. The most efficient adsorbent for ammonia is required for gas mask canisters, but the canisters for ammonia in the market are not necessarily satisfactory, because they serve only for shorter periods than the canisters for the other gases such as organic vapors, chlorine and sulfur dioxide.

Here, a new kind of adsorbent for ammonia was developed from active carbon through the liquid phase oxidation followed by the impregnation with salts of Ni, Co and Cu. The adsorption capacities of the newly developed adsorbents were studied by the adsorption isotherm observations at 25°C in vacuum apparatus and compared with those of the other commercial adsorbents, original and impregnated with transitional metal salts.

Gas mask canisters packed with the metal impregnated oxidized active carbon were tested at the standard gas mask test conditions according to JIS* in comparison with the commercial ones.
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EXPERIMENTAL

Materials

The adsorbents submitted to the adsorption isotherm measurements for ammonia were as follows. Active carbon from Kuraray Chemicals Co. Ltd. (steam activated coconut-shell charcoal between 8~15 mesh), oxidized active carbon prepared from the above active carbon, silica gel and alumina gel from Nishio Kogyo Co. Ltd. (100 mesh) and aluminum oxide hydroxide used in a commercial gas mask canisters for ammonia. These adsorbents were impregnated with sulfates of Ni, Co and Cu in the laboratory.

The adsorbents examined as gas mask canisters for ammonia were active carbon and oxidized active carbon which were impregnated with copper sulfate.

Active carbon was oxidized in the laboratory as follows. Active carbon of 50 g was poured into 250 ml of 14 N nitric acid solution at 105°C or of 7 N nitric acid solution at 95°C respectively and the temperature was maintained constant for various times up to 5 hr. Then the mixture was drained on glass fiber filter. The product was washed with de-ionized water until the supernatant of the rinsing water gave less conductivity than 0.2 μΩ⁻¹ and freeze-dried.

The above adsorbents were impregnated with sulfates of nickel (II), cobalt (III) and copper (II) as follows; each adsorbent was dipped in the salt solutions of various concentrations up to the saturation for 1 day at room temperature and then drained on filter paper and freeze-dried. The amounts of metals carried by the adsorbents were determined by atomic absorption spectroscopy on the acidic extracts which were obtained from the metal impregnated adsorbents.

Methods

Adsorption isotherms of ammonia on the adsorbents were measured by gravimetry using a quartz spring balance in a glass vacuum vessel. A specimen of the adsorbents was packed in a quartz container, hung on the balance, pre-evacuated at 10⁻³ Torr for 2 hr at room temperature and then contacted with ammonia at 25°C. The amount of adsorbed ammonia by the adsorbent and the equilibrated pressure were plotted.

Gas mask canisters of chokketsu-shiki-kogata type were packed with about 82 g of active carbon and oxidized active carbon and with about 88 g of metal impregnated oxidized active carbon respectively. They were tested in the conditions according to JIS.¹ That is, an air stream at the flow rate of 30 l/min was generated and conditioned at 25°C and 50% of relative humidity and mixed with ammonia to the concentration of 0.1%, which was introduced to a canister set in a thermostated air bath at 25°C. The leakage of ammonia in the effluent air stream from the canister was detected with phenolphthalein.
RESULTS

The adsorption isotherms of ammonia on various adsorbents at 25°C were shown in Fig. 1. Ammonia is intrinsically little adsorbed by active carbon. By the liquid phase oxidation, active carbon was improved to adsorb ammonia and it reached to have the larger adsorptivity than silica gel and a commercial adsorbent used in a gas mask canister (aluminum oxide hydroxide).

Metal salts carried by the adsorbents promoted the adsorptivity for ammonia. Among the three kinds of transitional metal salts, nickel salt was carried at the maximum amounts by all kinds of the adsorbents and promoted the adsorptivities to the largest extent. Fig. 2 shows the adsorption isotherms of ammonia on active carbon impregnated with metal salts of various amounts and Fig. 3 does the isotherms on the oxidized active carbon (prepared by oxidation of active carbon with 7 N nitric acid solution for 5 hr) carrying metals.

These adsorption isotherms were transformed into Langmuir's equation. They were expressed by almost straight lines in Langmuir's relation from which the amounts of ammonia to cover the surface of the adsorbents by monolayer were calculated. Fig. 4 shows the amounts of ammonia adsorbed at monolayer in relation with the amounts of metals impregnated on the adsorbents. As seen in the figure, active carbon, original and oxidized, are both promoted as ammonia adsorbent by the metal impregnation and nickel.

Fig. 1. Adsorption isotherms of ammonia on various kinds of adsorbents at 25°C. Oxidized active carbons were prepared from active by treating with 7N nitric acid solution for 5 hr or with 14N nitric acid solution for 3 hr respectively.
Fig. 2. The effect of metal impregnation of active carbon on adsorption isotherm of ammonia at 25°C. The amounts of metals impregnated on active carbon were presented in parenthesis.

Fig. 3. The effect of metal impregnation of oxidized active carbon on the adsorption isotherm of ammonia at 25°C. The amounts of metals impregnated on the oxidized active carbon were presented in parenthesis. The oxidized active carbon was prepared from active carbon by treating with 7N nitric acid for 5 hr.
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Fig. 4. The relations between the amounts of metals retented by the adsorbents and the amounts of ammonia adsorbed on them at Langmuir's monlayer at 25°C.

- ● Active carbon
- ○ Oxidized active carbon
- □ Silica gel
- △ Alumina gel

salt is most effective for this purpose. Silica gel and alumina gel were similarly improved by the metal impregnation, especially with nickel. Among these adsorbents, the largest adsorptivity for ammonia was found on nickel impregnated oxidized active carbon on which 9.4 mmol/g of ammonia was adsorbed to cover the surface by monolayer. It is larger than the amount of ammonia adsorbed by the adsorbent currently used in gas mask canisters.

The test of the service lives of the canisters showed that the canisters packed with cupper impregnated oxidized active carbon served for longer periods than those in the market. That is, the canisters packed with active carbon oxidized with 7 N nitric acid solution for various times up to 5 hr served for the periods up to 36 min as shown in Fig. 5 which do not satisfy the requirement of JIS. When the oxidized active carbon impregnated with cupper was packed in the canisters, they served for 65 min in average. Their service lives are longer than the required one by JIS and longer than those of the commercial canisters of the same type (They serve for around 55 min). The canisters packed with active carbon, not oxidized but only impregnated with cupper sulfate, served for about 46 min. This service life would be brought about by the metal retented by active carbon and not by the active carbon itself.
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The results shown in Fig. 4 and 5 indicate that the surface acidity of the active carbon and the metals carried by the active carbon would act additively for ammonia adsorption.

**DISCUSSION**

The adsorbents currently used for ammonia are classified into two categories; one is acidic solids such as silica gel, aluminum oxide hydroxide and sulfonated coal and the other is transitional metals carried by solid granules such as cupramite. The adsorbents in the former category adsorb ammonia by acid-base interaction and those in the latter do by the formation of complex salts between ammonia and the metals. Active carbon itself does not adsorb ammonia though it is composed of well developed
microporous structure, because the surface is not acidic. Metal impregnated oxidized active carbon seems to belong to both of these categories.

In the previous study about the oxidized active carbon, the author showed that appreciable amount of strongly and weakly acidic groups were formed on the surface of active carbon by the liquid phase oxidation (up to about 7.3 meq/g of acidic groups with pKa < 11.0) and consequently active carbon was changed into an acidic porous adsorbent. The amount of the acidic groups on the oxidized active carbon increased along with the time of treatment of active carbon in the oxidizing solution while the specific surface area decreased. As the experimental result, the amount of adsorbed ammonia on the oxidized active carbon, from the adsorption isotherm measurements, increased when active carbon was oxidized with 14 N nitric acid solution for up to 3 hr and then decreased when the treatment was performed for the longer period. The amount of ammonia adsorbed at monolayer coverage on the original active carbon was negligible and it reached to 8.4 mmol/g on the carbon treated with 14 N nitric acid solution for 3 hr. When active carbon is treated with more dilute nitric acid solution, the changes of the carbon with the treatment progress more slowly. The initial slopes of the adsorption isotherms were steeper for the oxidized active carbon treated for longer period in nitric acid solution, which is beneficial to the adsorption of ammonia at very low concentration in the air.

By the metal impregnation, the adsorptivity of the oxidized active carbon for ammonia was further promoted. The extent of the adsorptivity elevation seems to be primarily related to the amount of the retented metals on the adsorbents, secondary to the kind of the carrier solids but not to the kind of the metals. The mole ratio of the retented metals on the adsorbents to the adsorbed ammonia at monolayer coverage falls in the range from 1:3 to 1:5. It is known that Ni(II), Co(III) and Cu(II) bind 4 or 6, 6 and 4 molecules of ammonia as ligand respectively. The results presented in Fig. 4 shows that the formation of the complexes between the metals and ammonia would be the mechanism to promote the adsorptivity for ammonia, though the reacting mole ratios did not reach those in the complete complex salts.

The test of gas mask canisters packed with cupper impregnated oxidized active carbon proved that the newly developed adsorbent could be used excellently as an adsorbent for gas masks. From the technical view, there would be possibility to obtain a better adsorbent than those tested here, because cupper impregnated oxidized active carbon is not the one having the largest adsorptivity among those presented in Fig. 4. Another possibility is also suggested from the results that efficient adsorbents for ammonia could be obtained by treating oxidized active carbon with the other transitional metals.

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