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Oxygen-plasma Treatment of Packing Materials for Gas Chromatography. The Incorporation of Oxygen into the Hydrocarbon Liquid Phase and the Formation of Crosslinked Products on the Support Surface

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(Received June 27, 1984)

The oxygen-plasma treatment of column packings for gas chromatography was examined with diatomaceous earth coated with several kinds of stationary liquid phases from the point of view of the modification of their chromatographic properties. A remarkable effect on the gas chromatograms of polar compounds was observed for the packings with nonpolar liquids, such as squalane and Apiezon L. The elimination of tailing and the improvement of the resolution by the plasma treatment were attributed to the incorporation of oxygen into the hydrocarbon liquids and the formation of crosslinked products covering the adsorptive support surface. These results were compared with the previous data on argon-plasma treatment.

Recently, we have examined the argon-plasma treatment of packing materials for gas chromatography.[1–3] It was found that the plasma treatment is effective for reducing the tailing of chromatographic peaks on several kinds of packings, such as squalane, Apiezon L, Silicone DC, and dioctyl phthalate on diatomaceous earth. The effect has been attributed to the formation of an inert coating on the adsorptive support surface. Because the distributed liquid of packings is thin and has a large surface area exposed to plasma, plasma treatment provides an effective means of modifying the chromatographic properties of the packings.

In the present study, the oxygen-plasma treatment of packings was undertaken in order to investigate its effect on gas chromatograms and the reactions in the stationary liquid phase caused by the oxidizing plasma. The results are compared with our previous data on the argon-plasma treatment.

Experimental

The column packings (60/80 mesh) were obtained from Wako Pure Chemical Industry. The apparatus and experimental details of the plasma treatment were described previously.[2] The oxygen-plasma treatment was carried out at a pressure of 0.1 Torr (13 Pa) by means of a radiofrequency generator operated at 13.56 MHz and with an output of 50 W. The gas-chromatographic test of the treated packing was also carried out as has been described previously; the packing was packed into a 1m×3mm i.d. stainless tube, and the nitrogen flow rate was 30 ml/min.

The molecular-weight distribution of the liquid extracted from the plasma-treated squalane on Chromosorb W was measured by means of a gel-permeation chromatograph (Toyo Soda HLC-801) in tetrahydrofuran (THF). A differential refractometer and two 2-ft columns, TSK-Gel G2000H8 and G4000H8, connected in series, were used for the measurement. The IR spectrum of the extracted liquid was recorded on a Hitachi Model 295 spectrometer using NaCl plates.

Results

A remarkable effect was observed on the gas chromatograms of polar compounds when the packings with nonpolar liquids, such as squalane and Apiezon L, were treated with the oxygen plasma. Figure 1 shows the gas chromatograms of alcohols and aromatic ketones on Chromosorb W (non-acid washed (NAW))

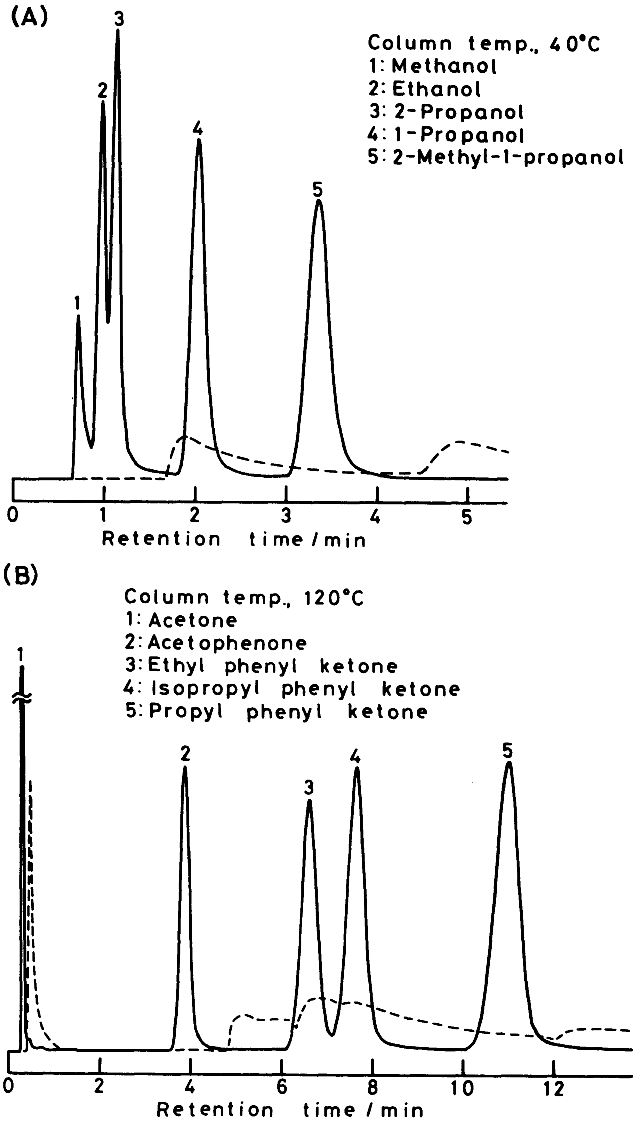

Fig. 1. Gas chromatograms on Chromosorb W (NAW) coated with 5% squalane: solid line, 10 min plasma treated; dotted line, untreated.

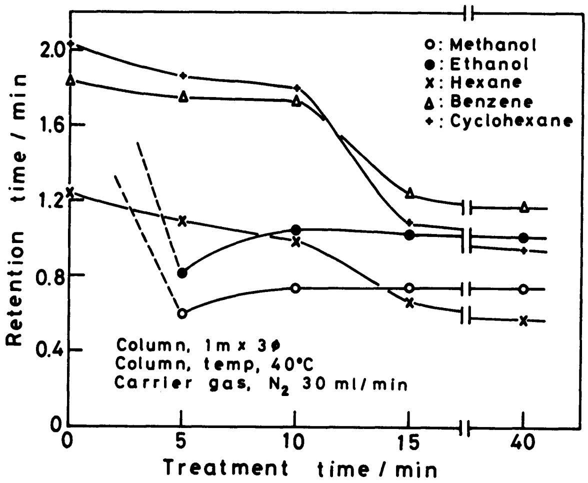

Fig. 2. Change in retention time by plasma treatment.

coated with 5% squalane before (dotted line) and after (solid line) the plasma treatment for 10 min. Sharp and well-separated peaks are obtained on the plasma-treated packing, whereas the peaks are very broad, with extensive tailing, on the untreated packing. The best peak separation was attained at the treatment time of 10 min. The changes in the retention times of several alcohols and hydrocarbons by the plasma treatment are compared in Fig. 2. The retention times of methanol and ethanol are significantly decreased during the first 5 min and then slightly increased during the next 5 min. On the other hand, the retention times of hexane, benzene, and cyclohexane slowly decreased with the increase in the treatment time. The effect of the plasma treatment was similar for 5% Apiezon L on Shimalite (NAW), as is illustrated in Fig. 3. By the plasma treatment, the retention time of ethanol is decreased much more than those of hexane and benzene, and the tailing of its peak is effectively reduced. Symmetrical and separated peaks are also obtained for the aromatic ketones on the plasma-treated packing.

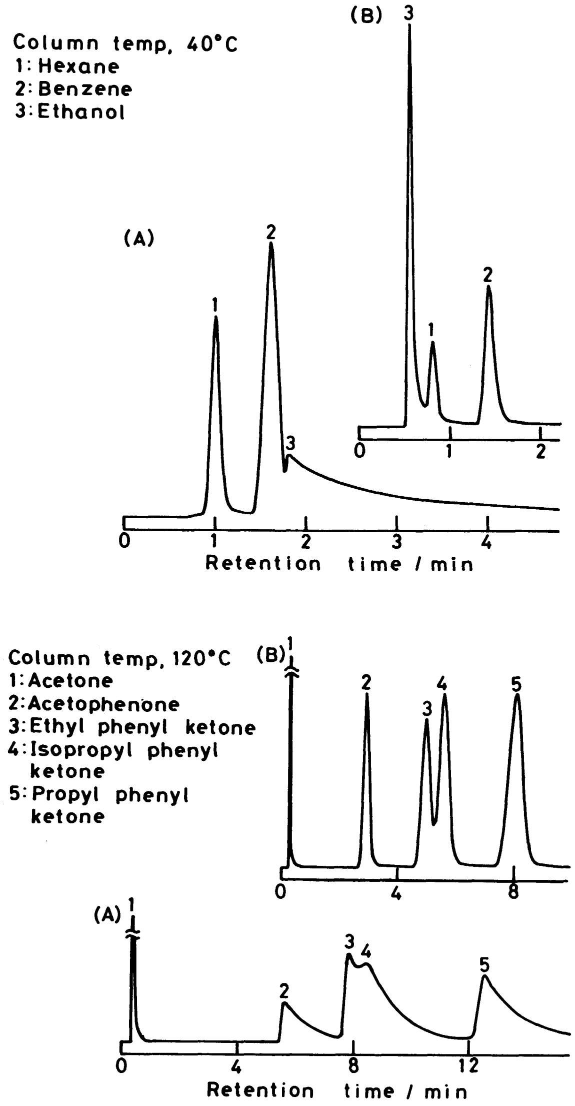

Fig. 3. Gas chromatograms on Shimalite (NAW) coated with 5% Apiezon L: (A) untreated; (B) 10 min plasma treated.

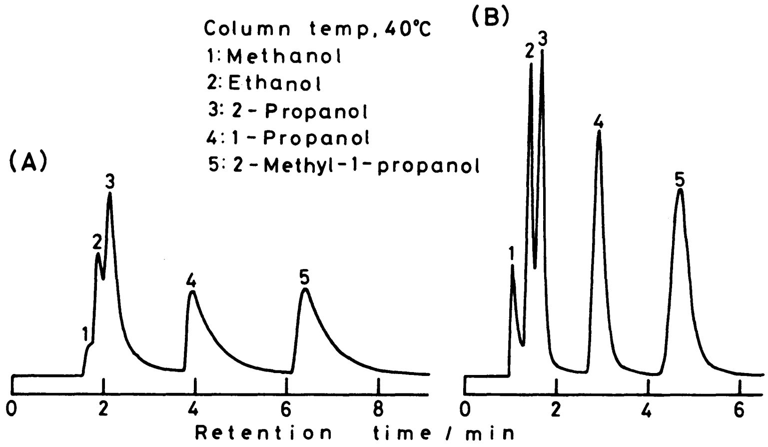

Fig. 4. Gas chromatograms on Chromosorb W (NAW) coated with 10% dioctyl phthalate: (A) untreated; (B) 10 min plasma treated.

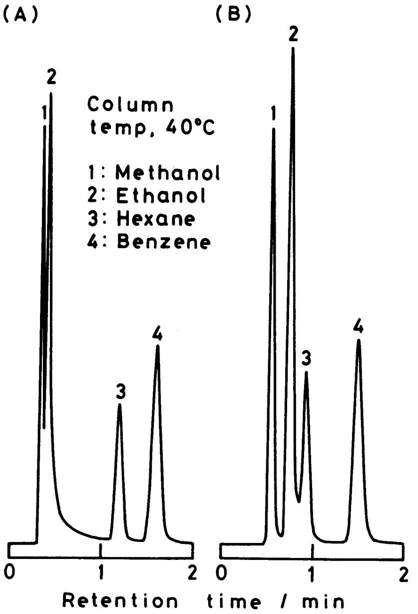

Fig. 5. Gas chromatograms on Chromosorb W (AW-DMCS) coated with 5% squalane: (A) untreated; (B) 10 min plasma treated.

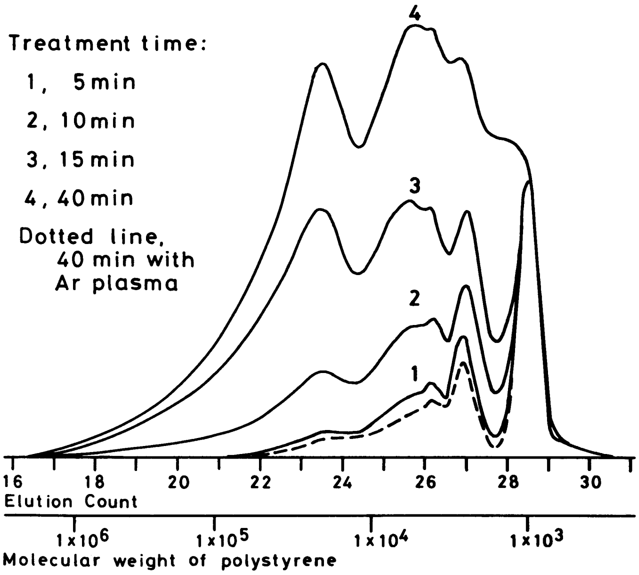

Fig. 6. Molecular weight distribution curves for liquids extracted from plasma treated packings (Chromosorb W (NAW) coated with 5% squalane).

Figure 4 shows the effect of the plasma treatment of Chromosorb W (NAW) coated with 10% dioctyl phthalate on the gas chromatogram of alcohols. Although the effect is less significant than those for the packings described above, the plasma treatment is effective for reducing the tailing. When packings coated with Silicone DC and polyethylene glycol were treated with the oxygen plasma for 10 min, only a slight decrease in retention time was observed, but there was no appreciable improvement in the resolution.

The oxygen-plasma treatment was also examined with acid-washed and dimethyldichlorosilane-treated (AW–DMCS) Chromosorb W coated with 5% squalane; the results are shown in Fig. 5. It can be seen that, by the plasma treatment, the retention times of methanol and ethanol are increased and the tailing of their peaks is eliminated. On the contrary, the retention times of hexane and benzene are decreased by the plasma treatment.

With a packing consisting of 5% squalane and Chromosorb W (NAW), experiments to elucidate the reactions caused by the oxygen-plasma treatment were carried out. After the plasma treatment, the distributed liquid was extracted from the packing with THF by using a Soxhlet extractor and refluxing for 5 h. The extract was submitted to gel-permeation chromatography. The molecular-weight distributions at different treatment times are shown in Fig. 6. These are normalized to the peak height at 28.5 counts corresponding to squalane itself. It is evident that the distributed liquid is polymerized during the plasma treatment. The yields of the higher-molecular-weight products increase with the increase in the treatment time. On the other hand, the formation of the polymerized products is limited in the case of the argon-plasma treatment, even at the longest treatment time examined, 40 min (dotted line).

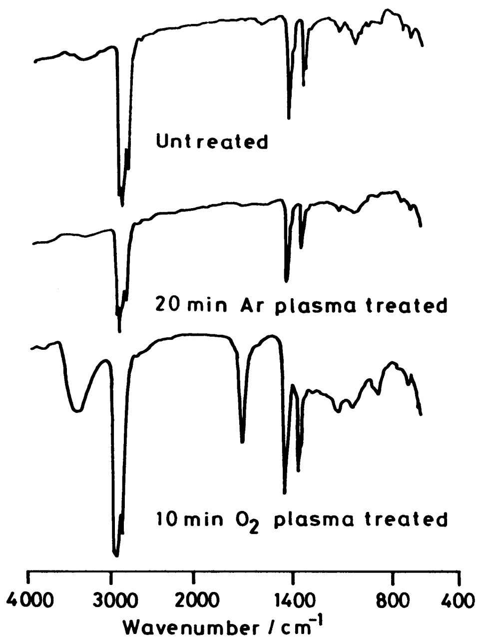

Fig. 7. IR spectra of the liquids extracted from packings (Chromosorb W (NAW) coated with 5% squalane).

The IR spectrum of the extracted liquid, which was measured after evaporating the THF from the extract, is shown in Fig. 7, together with those of the liquids extracted from the untreated and argon-plasma-treated packings. The IR spectrum for the oxygen-plasma treated packing shows the presence of carbonyl and hydroxyl groups, whereas there is no appreciable difference in the spectra between the untreated and argon-plasma-treated packings.

The support recovered from the packing by extract-

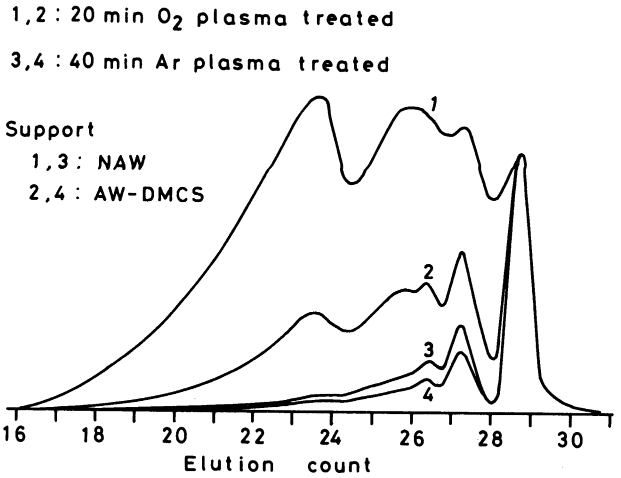

Fig. 8. Comparison of molecular weight distributions of extracted liquids for NAW and AW-DMCS supports.

ing the distributed liquid was dried under vacuum and then weighed to determine the weight loss of the packing due to the extraction. The weight loss decreased with the increase in the treatment time, much as in the case of the argon-plasma treatment,[2] indicating the formation of products not extracted with THF. The yield of such insoluble products, based on the distributed liquid, was 34.5% at a treatment time of 20min, which is comparable to that in the argon-plasma treatment, 31.7%.

For the sake of comparison, the molecular-weight distribution of the extracted liquid was measured for the packing with the AW–DMCS support. The formation of the soluble polymer depends on the support, as is shown in Fig. 8; that is, it is more pronounced on the NAW support in both the oxygen and argon-plasma treatments. Furthermore, the yields of the insoluble products remaining on the AW–DMCS support at the plasma-treatment time of 20min were 26.5 and 18.8% for the oxygen and argon-plasma treatments respectively. These yields are smaller than those on the NAW support.

Discussion

When a hydrocarbon substrate such as polyethylene is exposed to an oxygen plasma, the incorporation of oxygen and crosslinking are known to occur on the substrate surface.[4,5] Similar reactions are considered to occur in the hydrocarbon-liquid phase of the packing when it is treated with the oxygen plasma. The results for the packing with squalane demonstrate the incorporation of oxygen in the form of carbonyl and hydroxyl and the crosslinking to yield the high-molecular-weight products.

The formation of an inert coating on the support surface is considered to play an important role in the elimination of the tailing of chromatographic peaks, much as in the case of the argon-plasma treatment.[1–3] The yields of both the types of polymerized products, those extractable and unextractable with THF, on the NAW support were higher than those on the AW–DMCS support in the oxygen and argon-plasma treatments. Therefore, it seems likely that their formation is promoted by the NAW support surface and that the highly crosslinked products effectively cover it. It is also believed that the increase in the polarity of the liquid phase by the incorporation of oxygen reduces the adsorption of solutes on the support surface because of the increased interaction of the liquid with the support surface. Thus, the remarkable decrease in the retention times of the alcohols and aromatic ketones and the elimination of their tailing (Figs. 1 and 2) are attributable to the reduction of the support adsorptivity toward the solutes.

Another effect of the increase in the polarity of the distributed liquid is an increase in the retention times of the alcohols, resulting in a higher peak separation. This was observed for the packing with the NAW support during the second 5min of treatment (Fig. 2) and also for the packing with the AW–DMCS support (Fig. 5).

The formation of the soluble polymerized products was much more pronounced in the oxygen-plasma treatment than in the argon-plasma treatment. This can be explained by the reactions of oxygen with radical species inhibiting the crosslinking and/or initiating oxidative decomposition of the polymerized products.

This work was supported in part by the Shimadzu Co.

References

1) Y. Yamamoto, S. Oka, and K. Hayashi, *Chem. Lett.*, **1981**, 221.

2) Y. Yamamoto, S. Oka, and K. Hayashi, *Bull. Chem. Soc. Jpn.*, **55**, 441 (1982).

3) S. Oka, Y. Yamamoto, and K. Hayashi, *Bull. Chem. Soc. Jpn.*, **55**, 3496 (1982).

4) M. Hudis, "Techniques and Applications of Plasma Chemistry," ed by J. T. Hollahan and A. T. Bell, Wiley-Interscience, New York, N. Y. (1974), p. 113.

5) H. Yasuda, *J. Macromol. Sci., Chem.*, **A10**, 383 (1976).