ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 4, pp. 630–634. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © A.I. Klimuk, L.A. Obvintseva, A.D. Shepelev, V.L. Kuchaev, M.P. Dmitrieva, E.N. Ushakova, A.K. Avetisov, 2008, published in Zhurnal Prikladnoi Khimii, 2008, Vol. 81, No. 4, pp. 593–597.

PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

A Study of Sorption and Decomposition of Ozone on Microfibrous Filtering Materials

A. I. Klimuk, L. A. Obvintseva, A. D. Shepelev, V. L. Kuchaev, M. P. Dmitrieva, E. N. Ushakova, and A. K. Avetisov

Karpov Research Physicochemical Institute, Moscow, Russia

Received October 3, 2007

Abstract—Decomposition of ozone on commercial and pilot filtering microfibrous materials based on polymers, glass fibers, and carbonized polymeric fibers was studied.

DOI: 10.1134/S1070427208040113

In view of the wide use of ozone in chemical and pulp-and-paper industries, microelectronics, water treatment, and medicine, a topical issue is development of methods for decomposition of excess ozone, including those to be used in individual and collective means for protection of the human respiratory system in those case when the maximum permissible concentration (MPC) of ozone in air is exceeded. Ozone is commonly decomposed with heterogeneous catalysts containing metals, such as Cu, Mn, Co, Fe, Ni, Ti, and Ag, and their oxides in various ratios [1]. Combined filters have also received recognition. These filters contain, in addition to catalysts, various sorbents and fibrous materials: glass fibers, carbon fibers [2, 3], and polymeric materials used both as porous supports and as active ozone-binding reagents [4–7]. Ozone is bound with various cyclic polymers: polyarene esters and sulfur-containing polymers [4], thioesters [5, 6], unsaturated polycycloolefins, and nonbornene and its higher homologues: nonbornodiene and dicyclopentadiene [5, 6]. An ozone-binding polymer can be used in a combined filter as a powder, grains, films, coatings, and finely fibrous materials. An advantage of fibrous materials is their low hydrodynamic resistance, developed surface equally accessible to ozone molecules, and room working temperatures. At present, fibrous filtering materials are efficiently used to catch aerosol particles. Industrially manufactured polymeric microfibrous materials, Petryanov filters (PF), are in common use [8, 9]. These materials are readily available and inexpensive.

A topical task is to create fibrous filtering materials for air purification to simultaneously remove aerosols and gaseous impurities. So far, several brands of materials for catching of radioactive iodine and oxidation of carbon monoxide have been developed and studies are being performed to develop new sorption-filtration materials [10–12]. It is of interest to find out whether PF and other fibrous filtering materials can be used to bind ozone. A separate issue is a search for ozone-resistant filtering materials for air purification to remove aerosol impurities in the presence of high concentrations of ozone.

The aim of this study was to examine decomposition of ozone on microfibrous filtering materials of various types in the context of the problems mentioned above. As objects of study served commercial filtering materials and pilot materials synthesized at the laboratory of aerosols at Karpov Research Physicochemical Institute.

EXPERIMENTAL

Industrial Petryanov filters [FPA-15-2.0,[1] FPP-70-0.5 (EKhMZ, Elektrostal', Moscow oblast); FPSAN-70-0.5 (Esfil, Simolaye, Estonia)], pilot materials (FPAN-10-3.0, FPF42-10-3.0, FPS-15), ultrathin glass fibers, and carbonized microfibers were studied.

All the FP samples, except glass fibers, were fabricated by electroforming [8, 9, 13]. Carbonized fibrous materials were produced by carbonization of

---

[1] The first figure in the designation of a filter is the average fiber diameter in tenths of a micrometer, and the second figure is the resistance to an air flow in millimeters of water at a flow velocity of 1 cm s^{-1}.

Table 1. Parameters of the microfibrous filtering materials under study

Material	Composition	Average fiber diameter, μm	Packing density, %	Specific surface area, $m^2 g^{-1}$
FPP-70-0.5	Chlorinated polyvinyl chloride	5–7	2.5	0.7
FPA-15-2.0	Cellulose diacetate	1.4	2.5–3	1.3
FPAN-10-3.0	Polyacrylonitrile	1.0	3–4	Not measured
FPF42-10-3.0	Copolymer of tetrafluoroethylene with vinylidene fluoride	1.0	3–4	″
Glass fibers	Silicon, boron, aluminum, and calcium oxides	0.2	5	″
FPSAN-70-0.5	Copolymer of styrene wit acrylonitrile	5–7	2–4	0.67
FPS-15 (pilot sample)	Polystyrene	1.5	3	1.83
Carbonized fibers	Carbon	2.0	4–5	1.56

microfibers composed of a phenol-formaldehyde resin [12]. The specific surface area of the samples was determined by the BET method on the basis of adsorption of krypton, using the standard procedure [14]. Some parameters of the materials are listed in Table 1.

The decomposition of ozone on microfibrous materials was studied using the flow-through method [15]. A gas with a known content of ozone was passed through a tube with a material under study. The change in the content of ozone after passing the gas through the tube was used to find the amount of bound ozone. The initial mass of the samples under study was 0.2 g. A tube with an inner diameter of 0.4 cm was densely packed with the material, with a 5–7-cm-long layer obtained. Ozone was produced by the electrolysis method [16]. The concentration of ozone was found by iodometric titration, with optical UV spectroscopy used in separate experiments.

The experimental setup used in the study is schematically shown in Fig. 1. Electrolyzer *1* is made of molybdenum glass. As electrolyte *2* serves a $NaClO_4$ solution. Pt-electrode *3* serves as the anode, and Ni-electrode *4*, as the cathode. Ozone-containing oxygen is liberated at the Pt-electrode, and hydrogen, at the Ni-electrode. The anode and cathode spaces are separated by ion-exchange membrane *5*. To prevent warming-up of the electrolyte, the electrolyzer is cooled with tap water (jacket *6*). Ozone-containing oxygen is delivered from the electrolyzer into fluoroplastic tube *9* packed with the material under study, passes optical cuvette *10*, and comes to a flask with a KI solution *11*. The parts of the setup are connected by fluoroplastic tubes. The loss of ozone on this ma-

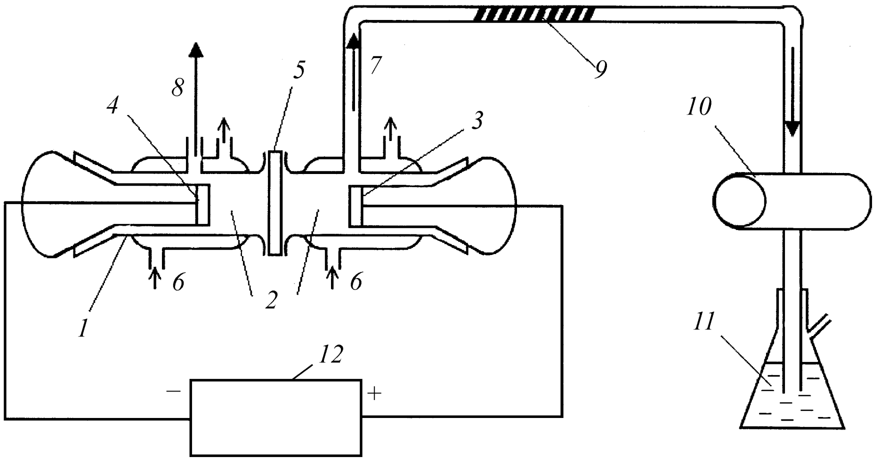

Fig. 1. Schematic of the experimental setup. (*1*) Electrolyzer, (*2*) 6 N solution of $NaClO_4$ electrolyte, (*3*) Pt-electrode, (*4*) Ni-electrode, (*5*) MF4SK (perforated ion-exchange membrane), (*6*) jacket, (*7*) O_3 + O_2 (gas), (*8*) H_2 (gas), (*9*) fluorioplastic tube with a material under study, (*10*) optical cuvette, (*11*) 0.05 N solution of KI, and (*12*) power unit.

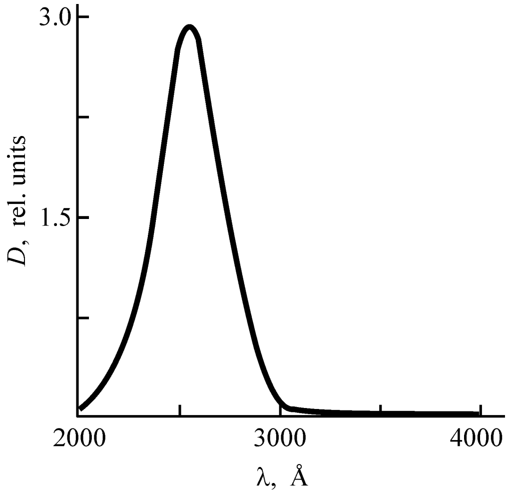

Fig. 2. UV absorption spectrum of ozone produced by electrolysis of a $NaClO_4$ solution. (*D*) Optical density and (λ) wavelength.

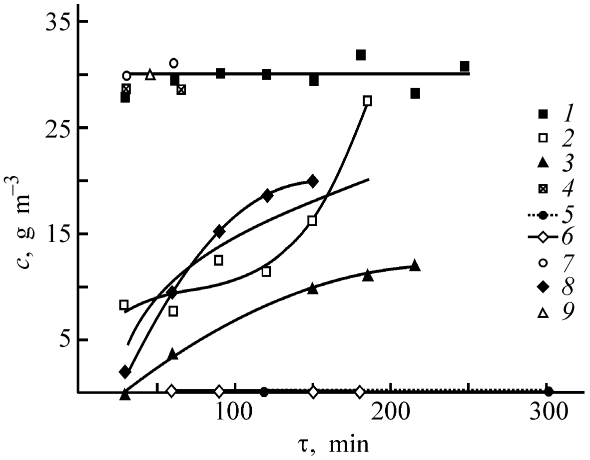

Fig. 3. Ozone concentration *c* after passing ozone-containing oxygen trough the layer of a material vs. time τ. (*1*) Empty tube, (*2*) FPP-70-0.5, (*3*) FPA-15-2.0, (*4*) FPAN-10-3.0, (*5*) FPS-15, (*6*) FPSAN-70-0.5, (*7*) glass fibers, (*8*) carbonized fibers, and (*9*) FPF42-10-3.0.

terial is insignificant because it has a small coefficient of heterogeneous decomposition of ozone [1, 17]. The tubes used in the experiments were treated with ozone for 1 h for passivation.

A UV spectrum of the ozone being formed, measured with a Perkin Elmer UV spectrometer in the range 2000–4000Å, is shown in Fig. 2. In this spectral range, only the characteristic absorption band of ozone, peaked at 2540 Å (Hartley band [18]), is present. It also follows from Fig. 2 that no chlorine dioxide (absorption band peaked at 3600 Å [18]) is formed in electrolysis of the $NaClO_4$ solution.

The content of ozone in oxygen increases with the current through the electrolyzer. The electrolyzer can produce and ozone–oxygen mixture containing 20.6 to 33.2 g m^{-3} of ozone as the current strength is varied from 296 to 550 mA. The corresponding flow rate of the ozone–oxygen mixture varies within the range 1.22–2.27 ml min^{-1}. The experiments were performed at a current strength of 510 mA. In this case, the flow rate of the ozone–oxygen mixture was 2.0 ± 0.1 ml min^{-1}. The electrolyzer was calibrated by measuring the amount of ozone absorbed by the KI solution at the outlet of an empty fluoroplastic tube of the same size as that with the material under study. The amount of ozone absorbed at this current in the course of 30 min in each of the several runs corresponded to an ozone concentration of 30 ± 2 g m^{-3} or to a content of about 1.5 vol %. The error in determining the ozone concentration is due to a minor instability in the current through the electrolyzer at a stabilized voltage across the electrodes. On absorbing ozone, the KI solution became first yellow, and then brown. In the course of the experiments, the solution was titrated, with monitoring by changes in coloration.

Figure 3 shows how the average concentration of ozone (during sampling) at the tube outlet varies with time. Straight line *1* shows the ozone concentration at the outlet of an empty tube. It can be seen in Fig. 3 that, with FPSAN-70-0.5 (points *6*) and FPS-15 (points *5*) filters, there is no ozone at the tube outlet for 6–7 h. For glass fibers (points *7*) and FPF42-10-3.0 (points *9*) and FPAN-10-3.0 (points *4*) filters, the ozone concentration at the tube outlet is the same as that in the case of an empty tube. For FPP-70-0.5 (points *2*) and FPA-15-2.0 (points *3*) filters and carbonized fibers (points *8*), a noticeable concentration of ozone is observed at the tube outlet, but this concentration is considerably lower than that observed with an empty tube.

On the basis of the data presented, all the materials studied can be divided into three groups: (i) materials inert toward ozone, on which the conversion of ozone is lower than 10% during a whole day of operation; (ii) active materials providing an ozone conversion exceeding 90%; and materials with an intermediate activity. On the materials of the third group the ozone conversion decreases during the first hours of operation.

The most active in ozone decomposition are polystyrene-containing materials: FPSAN-70-0.5 and FPS-15. These materials were used in experiments in which their activity was studied as a function of the duration of treatment with ozone. The results of seven successive runs with FPS-15 are shown in

Fig. 4. The experiments were carried out during a working day, with intervals between the runs equal to 12 to 48 h. It can be seen that, during the first three runs, the filter bound the whole amount of ozone delivered to the filter. At the end of run no. 4, a measurable ozone concentration appeared at the tube outlet (curve *4*). At the beginning of run no. 5, the ozone conversion was about 100% during 4 h and decreased to 80% by the end of the day (curve *5*). A similar behavior was also observed in the subsequent runs. By the end of run no. *7*, the conversion decreased to 50%. Similar results were obtained with FPSAN-70-0.5 filter, but its activity decreased considerably faster than that of FPS-15 filter, which may be due both to the lower specific surface area of FPSAN-70-0.5 (Table 1) and to the presence of acrylonitrile inert toward ozone in this filter. The results obtained demonstrate that the activity of the polymer with respect to ozone decomposition decreases (poisoning) both irreversibly and reversibly. The irreversible poisoning occurs via chemical reactions between a polymer and ozone, with chemical bonds in the polymer ruptured [15, 19]. The reversible poisoning may be due to formation of intermediate oxygen-containing compounds on the surface, which prevent adsorption of ozone. In a break in operation, these compounds partly decompose.

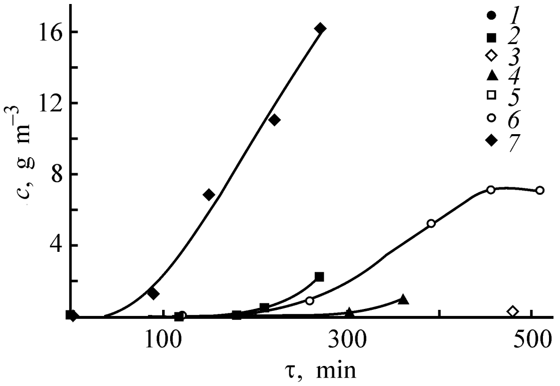

Fig. 4. Ozone concentration c after FPS-15 filter vs. time τ. *Digits at points* are run numbers.

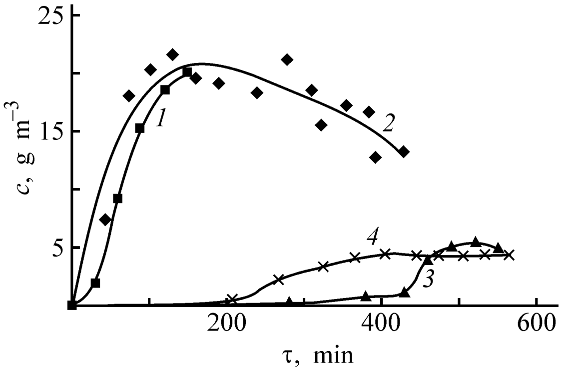

Fig. 5. Ozone concentration c after a layer of carbonized fibers vs. time τ. *Digits at points* are run numbers.

On the materials with an intermediate activity, the ozone decomposition was studied in detail on carbonized microfibers of phenol-formaldehyde resin. Four successive runs were made. Their results are shown in Fig. 5. In run nos. 1 and 2, the conversion decreased from 100 to 30% in 2 h of operation (curves *1*, *2*), but in run no. 2, the conversion gradually increased to 50% in the following 4 h. After a break of 4 days in run no. 3, a strong increase in activity was observed, so that the conversion was close to 100% during 7 h and then decreased to 80% (curve *3*). The next day, such a decrease in conversion occurred earlier (curve *4*). Thus, a complicated variation of activity was observed on carbonized fibers: under the action of ozone, the material of the filter is first deactivated and then activated. Possibly, the activation is partly due to loosening of the carbonized filter under the action of ozone and to an increase in its specific surface area.

Table 2 summarizes the results obtained in a study of the ozone treatment of microfibrous filtering materials with high and medium activity: data on the amount of ozone bound by a filter until its conversion decreases to below 90% and the corresponding duration of filter operation. A 0.2-g sample of FPS-15 filter worked for 40 h until the conversion reached 90% (inlet concentration 1.5%), with 0.15 g of ozone decomposed. The concentration of ozone in air at an MPC exceeded by an order of magnitude [19] is 4×10^{-5}%, i.e., a value four orders of magnitude lower than that in the experiments performed in this study. Under these conditions, the filter will provide a high conversion during a virtually unlimited time. This also refers to FPSAN-70-0.5 and FPA-15-2.0 filters.

Table 2. Experimentally observed efficiency of ozone catching by the materials under study

Material	Mass of ozone bound by a sample,* g	Duration of filter operation,* h
FPS-15	0.144	40
FPSAN-70-0.5	0.088	25
FPA-15-2.0	0.0066	2
Carbonized fibers	0.0018	18

* At an ozone conversion exceeding 90%.

CONCLUSIONS

(1) Analysis of the ozone decomposition on commercial and pilot filtering materials shows that filters based on polystyrene (FPS-15, FPSAN-70-0.5) exhibit a high activity in ozone binding; FPF42-10-3.0 and FPAN-10-3.0 filters and glass fibers are inert toward ozone; FPP-70-0.5 and FPA-15-2.0 filters and carbonized microfibers possess an intermediate activity.

(2) The activity of the polymeric filters decreases under the action of ozone and is partly restored in its absence. The activity of carbonized filters increases upon treatment with ozone.

(3) Carbonized fibers show a complicated variation of activity in ozone binding.

ACKNOWLEDGMENTS

The authors are grateful to E.M. Kasatkin and N.F. Potapova for the provided technique for production and titration of ozone and for detailed consultations in the course of the study and to N.V. Kozlova for measuring the UV absorption spectrum of ozone.

The study was financially supported by the International Scientific-Technological Center (grant no. 3288).

REFERENCES

1. Lunin, V.V., Popovich, M.P., and Tkachenko, S.N., *Fizicheskaya khimiya ozona* (Physical Chemistry of Ozone), Moscow: Mosk. Gos. Univ., 1998.
2. Varshavskii, V.Ya., *Uglerodnye volokna* (Carbon Fibers), Moscow: TIP VINITI, 2005.
3. US Patent 5 262 129.
4. US Patent 5 837 036.
5. US Patent 5 593 594.
6. US Patent 5 853 457.
7. US Patent 5 976 471.
8. Petryanov, I.V., Kozlov, V.I., Basmanov, P.I., and Ogorodnikov, B.I., *Voloknistye fil'truyushchie materialy FP* (FP Fibrous Filtering Materials), Moscow: Znanie, 1968.
9. Filatov, Yu.N., *Elektroformovanie voloknistykh materialov (EVF-protsess)* [Electroforming of Fibrous Materials (EVF Process), Moscow: Neft' i gaz, 1997.
10. Basmanov, P.I., Kirichenko, V.N., Filatov, Yu.N., and Yurov, F.L., *Vysokoeffektivnaya ochistka gazov ot aerozolei fil'trami Petryanova* (High-Efficiency Purification of Gases To Remove Aerosols with Petryanov Filters), Moscow: Nauka, 2003.
11. Koshcheev, A.P., Serzhantov, A.E., and Shepelev, A.D., *Tret'i Petryanovskie chteniya, 19–21 iyunya 2001 g., Trudy* (Proc. of Third Petryanov Readings, June 19–21, 2001), Moscow: RITs MGIU, pp. 148–154.
12. Budyka, A.K., Polevov, V.N., and Shepelev, A.D., Abstracts of Papers, *Mezhdunarodnaya nauchno-prakticheskaya konferentsiya "Aerozoli i bezopasnost'–2005", Obninsk, 24–28 oktyabrya 2005 g.* (Int. Sci.-Pract. Conf. "Aerosols and Safety–2005," Obninsk, October 24–28, 2005), Obninsk: FGOU GTsIPK, 2005.
13. Filatov, Yu., *Electrospinning of Micro- and Nanofibers: Fundamentals and Applications in Separation and Filtration Processes*, Budyka, A. and Kirichenko, V., Eds., New York: Begell House, 2007.
14. Braude, G.E., Semenova, T.A., and Markina, M.I., *Khimiya i tekhnologiya azotnykh udobrenii, Vypusk 12* (Chemistry and Technology of Nitrogen Fertilizers, Issue 12), Moscow: Goskhimizdat, 1961, pp. 67–75.
15. Razumovskii, S.D. and Zaikov, G.E., *Ozon i ego reaktsii s organicheskimi soedineniyami (kinetika i mekhanizm)* [Ozone and Its Reactions with Organic Compounds (Kinetics and Mechanism)], Moscow: Nauka, 1974.
16. Potapova, F. and Rakov, A.A., *Elektrokhimiya*, 1971, vol. 7, no. 4, pp. 537–540.
17. Obvintseva, L.A., Chibirova, F.Ch., Kazakov, S.A., et al., *Sensors*, 2003, vol. 3, p. 504.
18. Okabe, H., *Photochemistry of Small Molecules*, New York: John Wiley and Sons, 1978.
19. Razumovskii, S.D., *Kislorod – elementarnye formy i svoistva* (Oxygen: Elementary Forms and Properties), Moscow: Khimiya, 1979.