Beiträge zur Tabakforschung · Band 7 · Heft 2 · Juni 1973 DOI: 10.2478/cttr-2013-0316

Study of Cigarette Smoke Filtration by Means of the Scanning Electron Microscope*

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INTRODUCTION

The optimum cigarette filter can be produced only after a thorough understanding of the filtration process is attained. A considerable amount of effort in fundamental research has given us some basic information about the filtration of aerosols by means of fibrous filters (1—3), and some of this information has resulted in the development of new filters or in the alteration of existing filters. Certain mathematical predictions concerning the extent and location of the deposition of aerosol particles on fibers were presented in some of these studies. Heretofore, a visual confirmation of these predictions had not been achieved. Several years ago, the light microscope was used to examine smoke deposits on filters (4), but the limited depth of field and lack of light absorption were serious handicaps of this technique. The scanning electron microscope overcame these handicaps, and it was used by *Keith* and *Mayer* (5) to examine smoke deposits on filters. However, some changes may have occurred in the fluid smoke deposits when the sample was placed in a vacuum bell jar and coated with metal to reduce charging effects during observation with the scanning electron microscope. The possibility of alterations in the smoke deposits was minimized by lowering the temperature of the used filter while it was in the vacuum coater (6). *Peck* described a novel technique in which a monomer vapor, which polymerized upon contact with the smoke sample, was used to form a stable film over the fibers and smoke condensate (7, 8). The purpose of the work reported here was to extend this method to two techniques to determine how the particulate phase of cigarette smoke is deposited on filters and individual fibers. A technique for coating individual smoke particles in the mainstream smoke was devised to observe these particles as they were intercepted by fibers.

EXPERIMENTAL

Apparatus and Reagents

Cigarettes were smoked on a single-port smoking machine designed in our Research Laboratories, and a Cambridge Stereo Scan Mark II scanning electron microscope was used to observe the filters and individual fibers. Methyl 2-cyanoacrylate vapor was used to coat the smoke particles. All filters used were of cellulose acetate and were prepared at Tennessee Eastman Company.

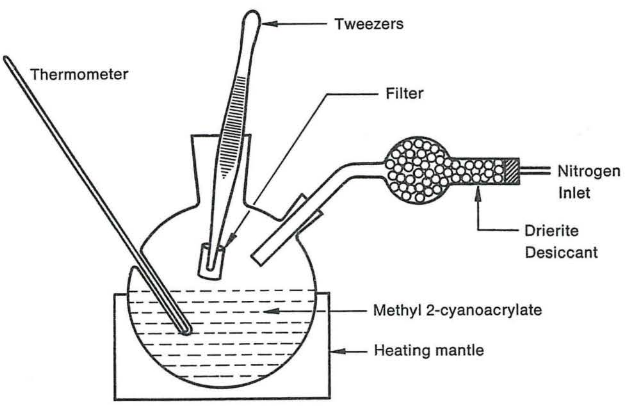
Procedure

All cigarettes were conditioned at 60 % relative humidity and 75° F before they were smoked under standard conditions (one 35-ml, 2-sec. puff/min.).

Two techniques were used to determine how the particulate phase of smoke is deposited on cellulose acetate filters and cellulose acetate fibers within a filter.

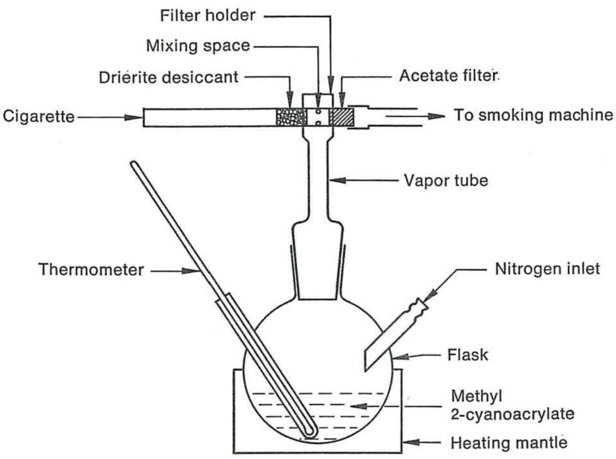
Technique A — Coating of Smoke Deposits on Filters: The technique of coating the specimen with a monomer vapor, which polymerizes to form a thin film over the smoke deposits, was described in an earlier publication (8). All samples described in this work were exposed to methyl 2-cyanoacrylate vapor which polymerizes upon contact with a weak Lewis base, such as water. Fifty milliliters of methyl 2-cyanoacrylate were added to a 100-ml flask equipped with a thermometer well (Figure 1). The monomer was heated to 70° C, and dry nitrogen was slowly passed through the flask. Immediately after the cigarette was smoked, the filter was removed from the cigarette and slit longitudinally with a razor blade. The filter was quickly exposed to the methyl 2-cyanoacrylate vapor for 5 sec. Then, the filter was placed in a vacuum coater where Au-Pd alloy was evaporated onto the filter to reduce static

Figure 1. Apparatus for coating cigarette filters.



* Received for publication: 17th November, 1972.

Figure 2. Apparatus for coating cigarette smoke particles.



effects in the scanning electron microscope (SEM). This technique produced a uniform film over the entire specimen. All photomicrographs were taken with the filter specimens placed at 30° from the horizontal.

The technique just described was also applied to individual fibers of cellulose acetate which were oriented either perpendicularly or parallel to the smoke stream in a hollow plastic tube. The tube was attached to a cigarette, and after the cigarette was smoked, the entire tube was exposed to methyl 2-cyanoacrylate vapor.

Technique B — Coating of Smoke Particles in Mainstream Smoke: The apparatus shown in Figure 2 was used to coat individual smoke particles with methyl 2-cyanoacrylate vapor before they were trapped by a filter. The filters for this purpose were specially constructed from a 30-mm plastic tube. A 10-mm section containing 200 mg of Drierite desiccant was placed next to the tobacco. The center section consisted of a hollow mixing chamber containing vent holes where monomer vapor entered the smoke stream. This section was adjusted to give approximately 50% dilution of the smoke. The last segment contained the filter of interest, either a 10-mm cellulose acetate filter or a single cellulose acetate fiber attached to the tube. The cigarette was placed in the coating device and the methyl 2-cyanoacrylate was heated to 70° C. As each puff (35 ml) of smoke was taken, a similar volume of methyl 2-cyanoacrylate vapor entered the mixing chamber, coated the smoke particles, and polymerized. The coated particles were subsequently trapped by the fibers. The outer segment of the filter was removed, coated with Au-Pd alloy, and observed in the SEM.

RESULTS AND DISCUSSION

Technique A — Examination of Smoke Deposits on Filters

Technique A was used to coat the filter shown in Figure 3. This is a photomicrograph of the front (2 mm from the tobacco end) of a 3.3-den./fil., "Y"-cross-section filter after four puffs of smoke were deposited on it. Several things are obvious from this photomicrograph. First, most of the deposition occurred on the edges of the Y-cross-section fiber. Second, the smoke deposits flowed together to form what appears to be a viscous coating over the fiber. Last, in the valley of the Y-cross-section fiber, droplet formation is evident; many of these droplets appear to be about 1 μ in diameter. Diameters of 1 μ are larger than the average diameter of smoke particles; so, apparently, some agglomeration of these particles occurred in the 5 min. which elapsed from the first puff until the filter was coated.

Figure 3.

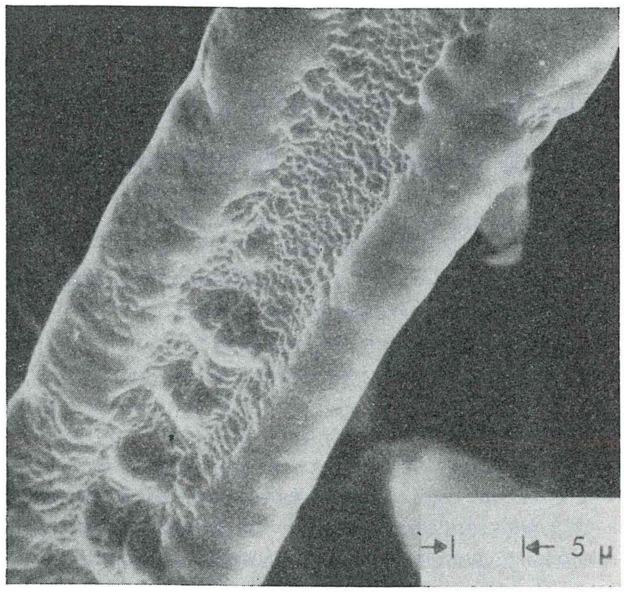


Figure 4 is also a photomicrograph of a 3.3 den./fil. filter which has four puffs of smoke deposited on it; however, the midpoint of the filter (a point 10 mm from the tobacco end) instead of the front is shown here. The fiber is less heavily coated than the one shown in Figure 3, and the deposit appears to be less

Figure 4.

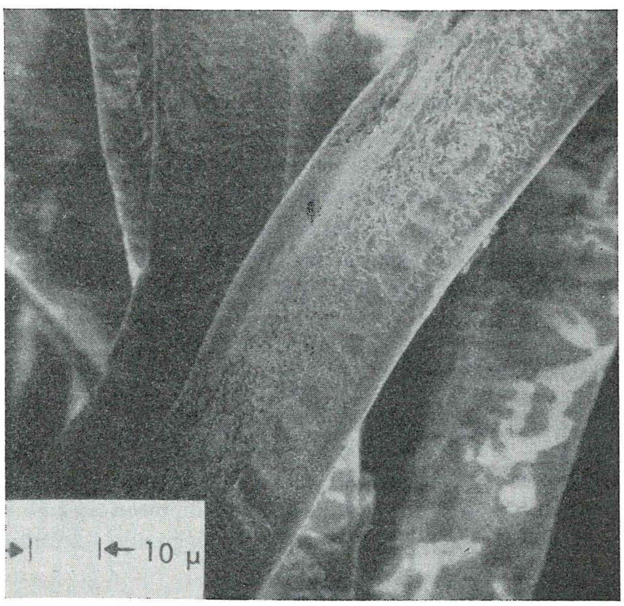


Figure 5.

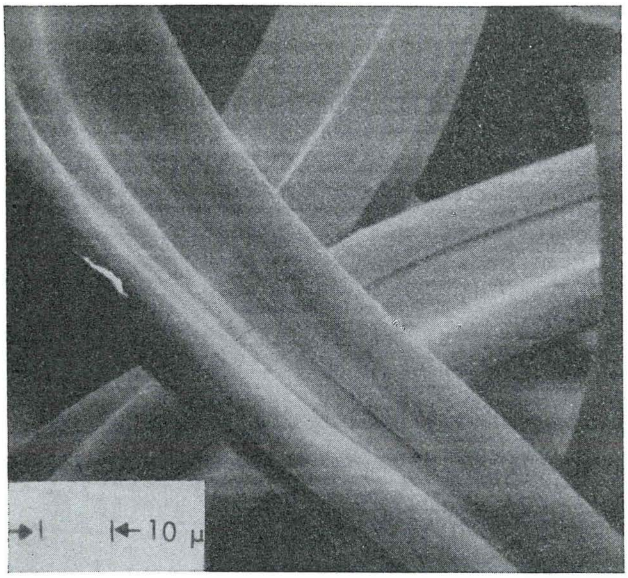


Figure 6.

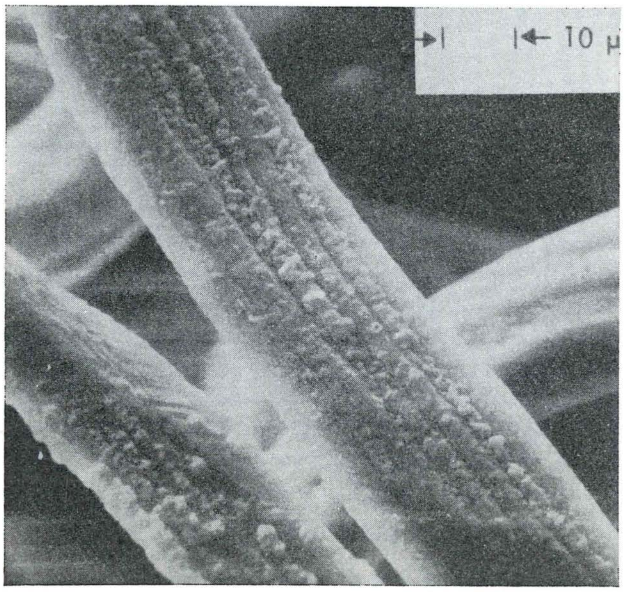


Figure 7.

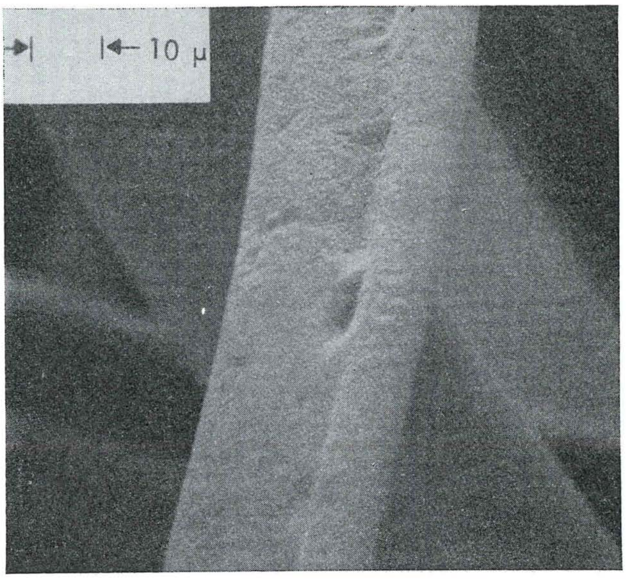
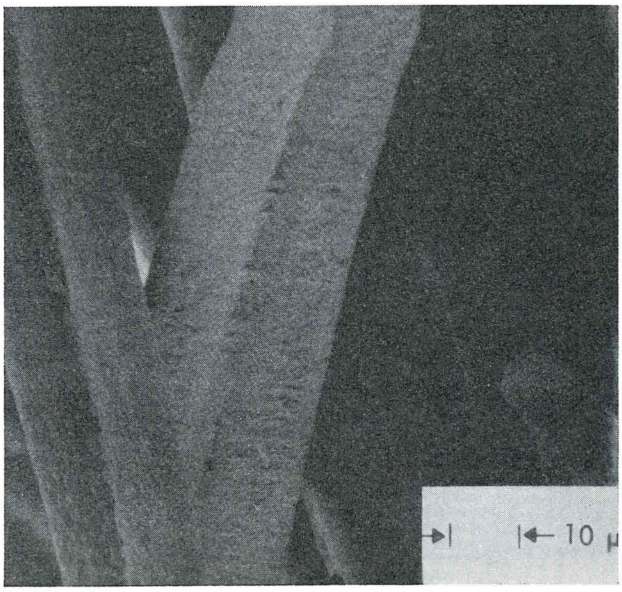


Figure 8.



viscous. This viscosity difference suggests a difference in the composition of the deposits throughout the length of the filter.

To determine if any of the previous deposits resulted from anomalies in the coating technique, an unused filter was subjected to technique A and observed with the SEM. This control filter is shown in Figure 5, and the photomicrograph shows none of the deposits present in Figures 3 and 4. The photomicrograph of this sample is not different from a photomicrograph of an uncoated filter.

Control samples, such as the one shown in Figure 5 were strained and abraded by hand so that the polymeric coating was fractured. These fractures and cracks in the coating were observed with the SEM, and the film thickness was estimated to be 0.05 μ. Similarly, samples containing smoke deposits and the polymer coating were manipulated to fracture the entire deposit. Near the tobacco end of the filter, the deposits from four puffs of smoke were approximately 1 μ thick. Thus, the thickness of the polymer coating is insignificant compared with the thickness of the deposits.

Figure 6 shows the deposits on a 1.6-den./fil., regular-cross-section cellulose acetate filter. The filter was constructed so that more than the usual number of fibers were randomly oriented to the smoke stream. The photomicrograph shows the midpoint of the filter after four puffs of smoke were deposited. The filter is more uniformly coated and more heavily coated than the standard 3.3 den./fil. filter (Figure 4).

Figures 7 and 8 show smoke deposits on cellulose acetate filters from bright leaf and burley tobacco cigarettes, respectively. The pictures show subtle, but significant, differences between the two deposits. The deposits from the bright leaf tobacco smoke flow together while those from burley tobacco smoke remain in droplets.

Figure 9.

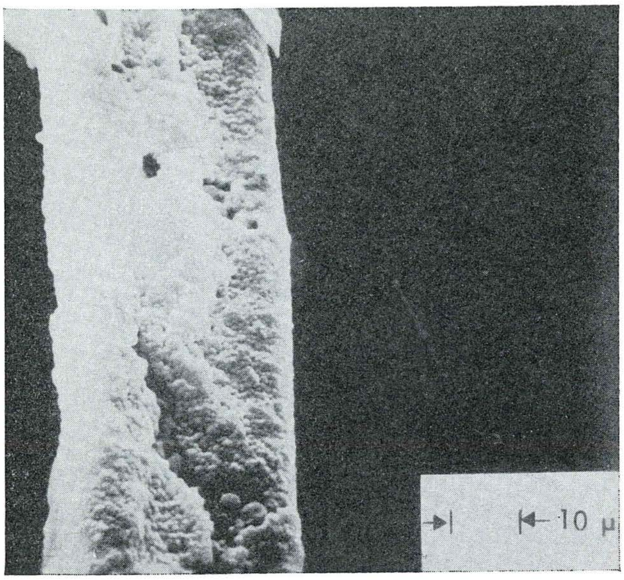


Figure 10.

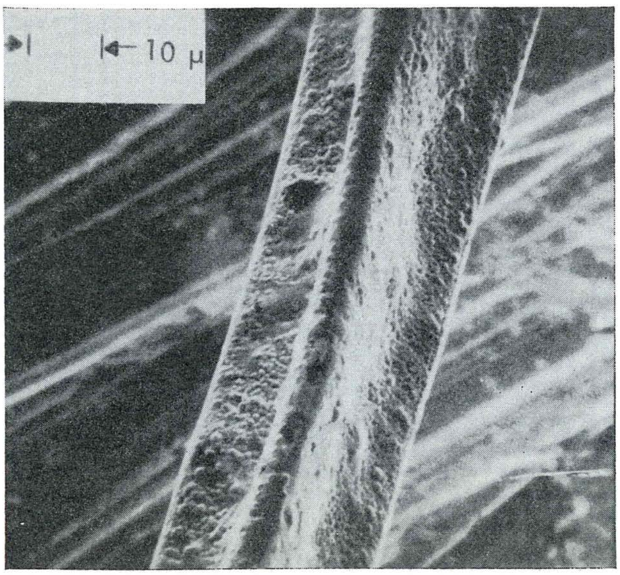


Figure 11.

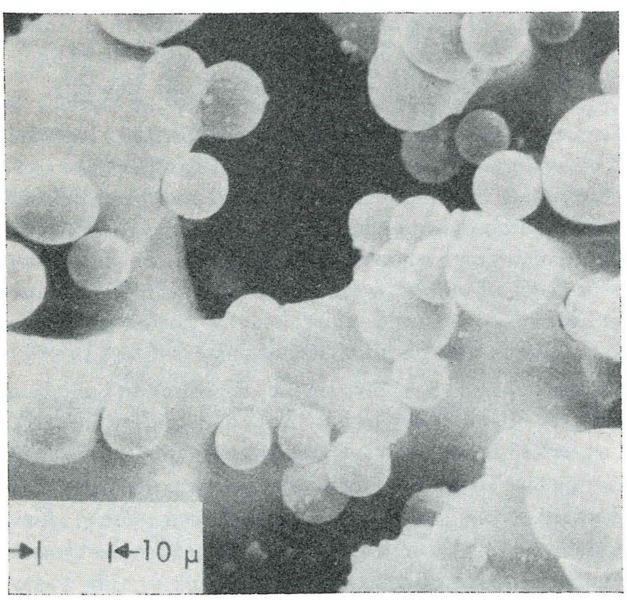
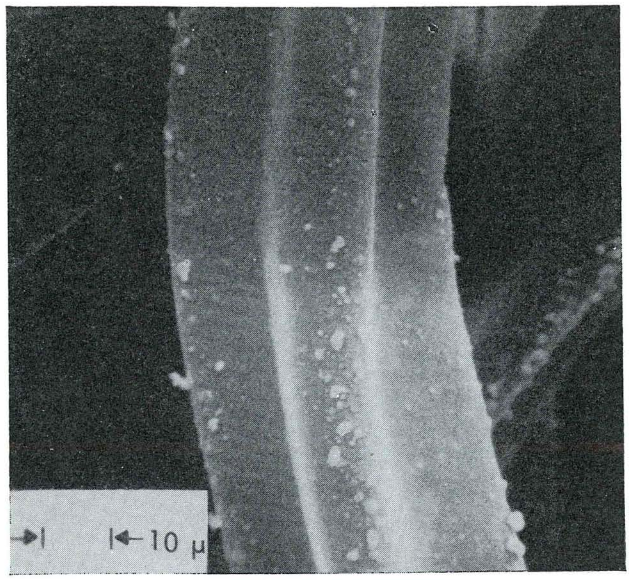


Figure 12.



Technique A — Examination of Smoke Deposits on Single Fibers

Smoke deposits on single cellulose acetate fibers oriented perpendicularly and parallel to the smoke stream are shown in Figures 9 and 10, respectively. The perpendicular fiber was attached to a hollow plastic tube (8 mm o. d.) which in turn was attached to a cigarette. A small copper wire was fastened to each end of a similar hollow tube, and the parallel fiber was attached to the midpoints of these two wires. The entire tube was attached to a cigarette and 10 puffs were taken. The most obvious difference between the two samples is the extent of deposition. The fiber oriented perpendicularly to the smoke stream is more heavily coated than the fiber oriented parallel to the smoke stream. In addition, the smoke droplets on the fiber in Figure 9 are larger than those on the fiber in Figure 10. This observation is consistent with the present theories of filtration. Diffusion is a more important mechanism than interception in the filtration of very small particles, and diffusion would be more likely to take place on the fiber parallel to the smoke stream than on the fiber perpendicular to the smoke stream. For large smoke particles, the perpendicular fiber should be a better filter than the parallel fiber since interception is more important than diffusion in the filtration of large smoke particles.

Technique B — Examination of Individual Smoke Particles on Filters

Technique B was first attempted with no drying agent between the entering smoke and the mixing chamber. The photomicrograph shown in Figure 11 resulted and was due to the polymerization of methyl 2-cyanoacrylate by excess water. Therefore, it was necessary to use the chamber containing Drierite desiccant (Figure 2) for all subsequent work. No more than two puffs of smoke could be taken before the desiccant was saturated and a photomicrograph similar to Figure 11 was obtained.

Figure 13.

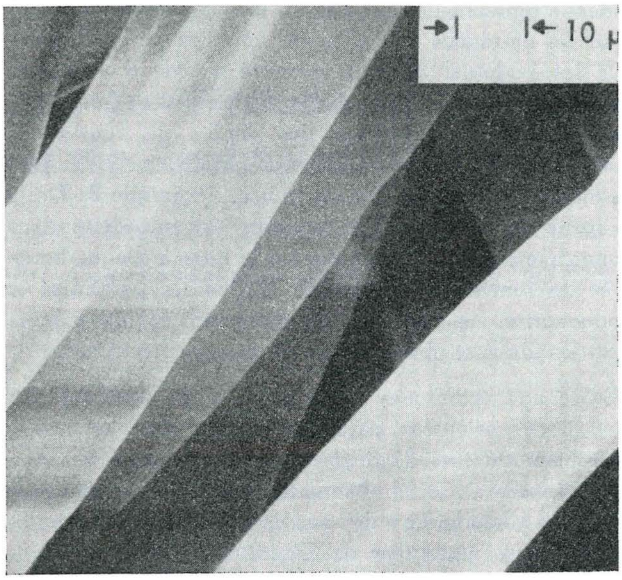


Figure 14.

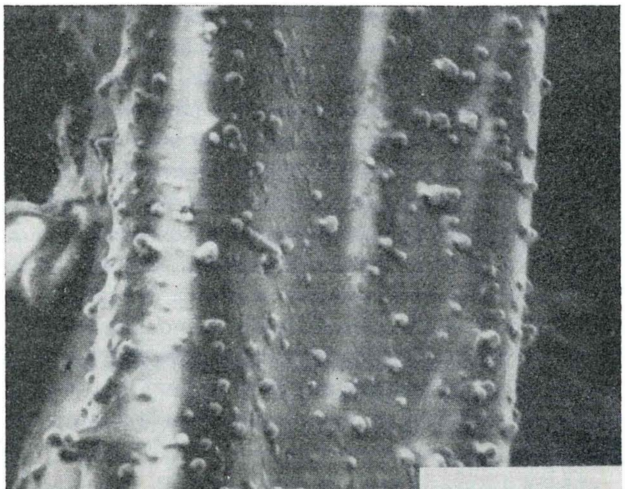


Figure 12 is a photomicrograph of the individual smoke particles trapped from one puff of smoke by a filter. The particles which range in size from less than 0.1 μ to 1 μ are trapped by the edges of the Y-cross-section fiber.

To determine if any of these particles came from the polymerization of methyl 2-cyanoacrylate rather than from smoke, the following control was used. A Cambridge filter was placed between the tobacco and the Drierite desiccant to remove the particulate matter but not the water vapor or vapor-phase components of the smoke. A photomicrograph of the control filter is shown in Figure 13 and proves that the particles present in the preceding photomicrograph are actual smoke particles.

Finally, technique B was applied to a single fiber, oriented perpendicularly to the smoke stream. The results are shown in Figure 14; at first glance, there appear to be too many large ($>$0.5 μ) particles on this fiber. Therefore, the particles which are 0.5 μ or larger in this 28-$\times$45-μ segment were counted, and the number of particles on the entire fiber was calculated to be 3.6×10^4. The number of particles in a single puff of smoke, the fraction of the total particles greater than 0.5 μ (9), the relative areas of the fiber and hollow tube, and the single fiber efficiency (3) were known; therefore, the total number of large particles ($>$0.5 μ) which should be present on the fiber could be calculated. A value of 2.9×10^4 was determined as the number of particles larger than 0.5 μ which should have been trapped on the fiber by the mechanism of interception. Impaction was shown to be unimportant in the filtration of cigarette smoke (3), and diffusion would contribute little to the removal of large particles by a perpendicularly oriented fiber. Therefore, the technique appears to be a valid one for maintaining the original form and location of the smoke particles. That is, the particles observed result from smoke and not from the coating material, methyl 2-cyanoacrylate. Furthermore, a visual confirmation of the single fiber efficiency was achieved with the technique.

SUMMARY

The method developed by *Peck* (8) for observing smoke deposits on cigarette filters with the scanning electron microscope was extended to two techniques to determine how the particulate phase of smoke is deposited on cellulose acetate filters and on individual cellulose acetate fibers. Technique A: Immediately after the smoke particles were deposited on the fibers, the filter was exposed to methyl 2-cyanoacrylate vapor; the methyl 2-cyanoacrylate monomer polymerized rapidly and formed a very thin film (0.05 μ thick) over the partially volatile particles so they could be examined in the vacuum chamber of the scanning electron microscope. This technique was used to observe smoke deposits on single fibers oriented either parallel or perpendicularly to the smoke stream. Technique B: Methyl 2-cyanoacrylate vapor was drawn into a mixing chamber in front of the filter as each puff of smoke was taken. The monomer coated the particles and polymerized. The coated particles were subsequently trapped by the fibers and observed with the scanning electron microscope.

From techniques A and B, it was observed that single fibers oriented parallel to the smoke stream showed a heavy deposition of small particles ($<$ 0.1 μ in diameter). This observation qualitatively confirms the theory that diffusion is one of the predominant mechanisms of filtration. Relatively small numbers of large smoke particles ($>$ 0.5 μ in diameter) were trapped by single fibers oriented perpendicularly to the smoke stream. These large particles were trapped by interception on fibers which were perpendicular to the smoke path. The edge of each Y-cross-section fiber, where interception is most likely to occur, was more heavily coated than other parts of the fiber. All of the large particles in a 28-$\times$45-μ area on a single fiber oriented perpendicularly to the smoke stream were counted. The total number of particles on the fiber were calculated and compared to the amount expected from the total number of particles per puff, the fraction of particles larger than 0.5 μ, and the single fiber efficiency. Good agreement between the experimental and calculated values was obtained.

ZUSAMMENFASSUNG

Die Arbeit berichtet über eine Erweiterung des Verfahrens, das *Peck* (8) zur rasterelektronenmikroskopischen Beobachtung von Rauchablagerungen in Cigarettenfiltern entwickelte. Hierdurch kann untersucht werden, wie sich die Partikelphase des Rauches im Zelluloseacetatfilter und auf den einzelnen Zelluloseacetatfasern niederschlägt. Verfahren A: Unmittelbar nach der Ablagerung der Rauchpartikel auf den Fasern wird der Filter gasförmigem Methyl-2-cyanakrylat ausgesetzt; das Monomer dieser Verbindung polymerisiert schnell und legt sich als sehr dünne Schicht (0,05 μ) um die teilweise flüchtigen Partikel, so daß diese in der Vakuumkammer des Rasterelektronenmikroskops untersucht werden können. Diese Methode wurde benutzt, um Rauchablagerungen auf einzelnen, parallel oder vertikal zum Rauchstrom gelegenen Fasern zu untersuchen. Verfahren B: Gasförmiges Methyl-2-cyanakrylat wird bei jedem Zug in eine vor dem Filter liegende Mischkammer gesaugt. Das Monomer überzieht die Partikel und polymerisiert. Die beschichteten Partikel werden dann durch die Filterfasern aufgefangen und mit dem Rasterelektronenmikroskop beobachtet.

Durch die Anwendung der beiden Verfahren A und B konnte gezeigt werden, daß sich kleine Partikel (Durchmesser: < 0,1 μ) in starkem Maße auf einzelnen Fasern niedergeschlagen hatten, die parallel zum Rauchstrom gelegen waren. Diese Beobachtung bestätigt in qualitativer Hinsicht die These, nach der die Diffusion einer der vorherrschenden Mechanismen des Filtrationsprozesses ist. Verhältnismäßig wenig große Rauchpartikel (Durchmesser: > 0,5 μ) wurden von vertikal zum Rauchstrom gelegenen Fasern aufgefangen. Besonders an den Kanten der Fasern mit Y-förmigem Querschnitt, wo die Ablagerung am wahrscheinlichsten ist, zeigte sich eine stärkere Beschichtung als auf den übrigen Teilen der Faser. Die großen Partikel, die sich auf einer einzelnen, vertikal zum Rauchstrom gelegenen Faser auf einer 28×45 μ großen Fläche abgelagert hatten, wurden gezählt. Die sich rechnerisch ergebende Gesamtpartikelzahl je Faser wurde mit der zu erwartenden Gesamtpartikelzahl je Zug, mit dem Anteil der Partikel, die größer als 0,5 μ sind, und mit dem Filtrationsvermögen der einzelnen Faser verglichen. Die experimentellen Ergebnisse stimmten mit den berechneten Werten gut überein.

RESUME

La méthode mise au point par *Peck* (8), pour observer les dépôts de fumée sur filtres de cigarettes à l'aide d'un microscope électronique à balayage a été étendue à deux techniques, permettant de déterminer comment la phase particulaire de la fumée est déposée sur des filtres d'acétate de cellulose, et sur les fibres isolées d'acétate de cellulose. Technique A: Immédiatement après le dépôt des particules de fumée sur les fibres, le filtre est exposé à la vapeur de méthyl-2-cyanoacrylate; le monomère de méthyl-2-cyanoacrylate se polymérise rapidement et forme un film très mince (0,05 μ) sur les particules partiellement volatiles, ce qui permet de les examiner dans la chambre à vide d'un microscope électronique à balayage. On a utilisé cette technique pour l'observation des dépôts de fumée sur des fibres individuelles orientées parallèlement ou perpendiculairement au flux de fumée. Technique B: De la vapeur de méthyl-2-cyanoacrylate est introduite dans une chambre de mélange devant le filtre à chaque bouffée de fumée. Le monomère enrobe les particules et polymérise. Les particules enrobées sont ensuite piégées par les fibres et observées au microscope électronique.

Grâce aux techniques A et B on a pu observer que les fibres orientées parallèlement au flux de fumée portaient un fort dépôt de petites particules (< 0,1 μ de diamètre). Cette observation confirme qualitativement la théorie qui dit que la diffusion est un des mécanismes principaux de filtration. Un nombre relativement restreint de grandes particules de fumée (diamètre > 0,5 μ) ont été piégées par des fibres orientées perpendiculairement au flux de fumée. Les grandes particules ont été piégées par interception par des fibres perpendiculaires au chemin de la fumée. Les angles de chaque fibre, de coupe en forme de Y, où l'interception avait le plus de chances d'apparaître, étaient plus garnis que les autres parties de la fibre. Sur une surface de 28 sur 45 μ d'une fibre unique orientée perpendiculairement au flux de fumée, on a compté le nombre total de grandes particules. Le nombre total de particules sur la fibre a été calculé, et comparé au nombre prévu à partir du nombre total de particules par bouffée, la part de particules plus grandes que 0,5 μ, et l'efficacité d'une fibre isolée. On a obtenu un bon accord entre la valeur calculée et la valeur observée.

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