Vapor Filtration by Fibrous Cigarette Filters*

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Over a period of years, the composition and properties of cigarette smoke have been studied by a number of workers within and without the tobacco industry. These studies have created a desire for modifying the smoke stream issuing from a burning cigarette selectively. The principal goal has been to provide systems which would selectively remove components thought to be undesirable without detracting from the taste and satisfaction of the smoke stream. Among the possible routes towards such a goal, selectively operating filter systems have been extensively investigated. Such filters are designed to remove disproportionate amounts of some components from the smoke stream, and have generally fallen into two categories, solid adsorbent filters and modified fibrous filters.

The first category, solid adsorbent filters, utilize the well known adsorbent properties of materials such as charcoal to effect a selective removal of some gaseous or vaporous components of the smoke stream. The extensive surface area of these adsorbents, which is largely contained in a network of capillary pores throughout the solid, provides a favorable situation for the condensation of gaseous components within the material. Materials which have suitable vapor pressures for condensation on the extensive adsorbent surface can be effectively removed. Other materials which have little or no tendency to condense from the gaseous state onto the adsorbent surface, or are so non-volatile as to be largely condensed in the smoke particles are largely unaffected by the adsorbent. The net result is a selective removal of these materials of intermediate volatility. The selective filtering action of the adsorbent can be somewhat modified by altering the physical properties, amount, and chemical nature of the adsorbent surface.

Because of its extensive adsorbent capacity and relative insensitivity to water, charcoal has become the preferred adsorbent for cigarette filter use. In 1959, *Irby and Harlow* (1) described the performance of a charcoal cigarette filter, and since that time the action of a number of other charcoal filters has been described in the literature (2, 3, 4). These studies have shown that efficient carbon filters remove from 50 to 95% of a broad spectrum of materials with boiling points between room temperature and 175° C. Examples of such materials are isoprene, acetaldehyde, acrolein, benzene, toluene, biacetyl and furfural.

This similarity of action for a wide variety of materials of similar volatilities is one of the chief drawbacks of charcoal filters. The essentially physical adsorption operating in these filters does not allow them to differentiate chemically between those volatile compounds which are undesirable because of their irritating properties and those which are desirable because of their taste and aroma properties.

The second category of selective filter systems is that of fibrous or modified fibrous filters. Although fibers have an extensive external surface, which makes them good particulate filters, they lack the internal capillary structure of charcoal, so that their overall surface area is of a lower order of magnitude. They, however, can offset this by providing a strong affinity for specific smoke components. These in general are materials which are readily soluble in or chemically interact with the unmodified or modified fiber. Because of the lower surface of fibrous filters when compared to charcoal, they are found to operate best selectively on materials of quite low but still appreciable volatility which are readily condensable both on the filter media and in the passing smoke particles.

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These materials are generally distributed between the vapor and particulate phases. Consequently, their selective removal is thought to occur through a largely irreversible condensation of them from the vapor phase and a retardation of evaporation of them from previously captured smoke particles by their interaction with the filtering material.

Examples of materials susceptible to removal by fibrous filters are water and phenol. The removal of water has been studied by *Waltz and Häusermann* (5) among others. Their data indicate a changing pattern of water removal ranging from a non-selective removal in early puffs to a significant selective removal during later puffs for cellulose acetate and cellulose filters. The overall selectivity is found to be slight for cellulose acetate filters and somewhat more marked for cellulose filters.

Phenol and its removal by fibrous filters have been extensively studied for over five years. A number of authors have examined a wide variety of filtering media for their ability to remove phenol selectively. These experiments have indicated that cellulose acetate possesses an essentially unique capacity for the removal of phenol from the smoke stream. This capacity is enhanced by the addition of plasticizing agents and other oxygenated liquid additives as indicated by *Spears* and others (6, 7, 8, 9).

From the preceding discussion, it is apparent that there are two general kinds of selective action in filters. One comes from the largely physical adsorption on solids of extensive surface area and the other comes from the stronger solvation or chemical interaction of selected materials with fibrous filters. Since the latter type of selectivity shows promise of being specific for particular chemical species, and since a greater range of additives can be conveniently applied to fibrous filters, it became of interest to investigate methods of extending the selective action of fibrous filters. To study this, a variety of liquid materials were applied to fibrous filters, and the removal of lower boiling vapor components was investigated. This paper summarizes these experiments and considers the relative importance of vapor transport to the filter surface, vapor sorption in the liquid coating, and vapor diffusion into the filter medium.

The experimental technique consisted of preparing filter samples from cellulose acetate cigarette tow coated with 0 to 60% added liquid. Two coating methods were employed, both being found to give equivalent results. The first, used for large samples, consisted of the normal spray application by means of a centrifugal plasticizer applicator on the filter rod-making machine. The second involved dissolving the additive in diethyl ether and soaking a previously prepared filter rod in the ether solution. The ether was subsequently evaporated leaving a filter rod uniformly coated with liquid additive. Treated filter samples, ranging in length from 20 to 50 mm, were tested either with a model gas system or by attachment to and smoking with an 85 mm commercial cigarette.

The model gas test consisted of passing an air-acetone mixture containing 100 to 1000 micromoles of acetone per liter through filter tips, and estimating the percent removal of acetone. This was accomplished by measuring the intensity of the 5.8 micron carbonyl peak of the inlet and outlet streams in a one meter gas cell on a Perkin-Elmer Model 137 infrared spectrophotometer. The model gas mixture was prepared by appropriate mixing of clean air and acetone saturated air streams, the mixture being passed through the filter tip at 17.5 ml/sec. Values from four to five measurements on a given tip were used to obtain average values of vapor removal for each filter sample tested.

The smoking tests involved the attachment of the experimental filters to weight selected 85 mm cigarettes and smoking them on a six-port smoking machine of the type recently described by *Newsome et al.* (10). In this smoking system, six cigarettes were simultaneously puffed upon to provide a common vapor sample, and the sample analyzed consisted of a mixture of the second through seventh puffs. This was achieved by lighting the cigarettes at one minute intervals. In all experiments a 35 ml puff of two seconds duration was utilized.

A five milliliter aliquot of the vapors passing through Cambridge CM-113 filter pads was directly injected onto the chromatographic column by means of a sampling valve. The chromatographic apparatus consisted of a Wilkens Aerograph, Model 1520, and Minneapolis Honeywell recorder. The column system contained 2 foot and 15 foot sections of 1/8 inch stainless steel tubing in series, the first containing diisodecyl phthalate on Chromosorb W, and the second 18% $\beta\beta'$ oxydi-propionitrile and 2% di(2-methoxyethyl) phthalate on Chromosorb W. Nitrogen flowing at a

rate of 30 ml/min. was used as a carrier gas. The program consisted of 5 min. at 25° C, 15 min. increasing to and holding at 55° C, 1 min. increasing to 67° C, 9 min. holding at 67° C, 1 min. increasing to 87° C, and holding at this temperature for the remainder of the run. The chromatographic system was designed for reasonably rapid analysis with moderate resolution of components, and yielded some 23 peaks within approximately 35 minutes. Figure 1 illustrates a representative chromatogram with tentative peak identification of the major components, as determined by retention time analyses.

FIGURE 1

Typical chromatogram of the vapor phase of cigarette smoke

Average peak heights were computed for 10 components of the mixture: isoprene, acetaldehyde, 2-methylfuran and propionaldehyde, methanol, acrolein, benzene, acetone, 2-butanone, toluene, and 2,3-butanedione. These were used to compute vapor retention efficiencies by comparison of vapor yields from treated filters and equivalently prepared and smoked untreated filter cigarettes. To provide an overall rating of vapor retention for various samples, the ten individual efficiencies were averaged.

In studying the removal of vapors by a filter system, it is desirable to consider first factors which would affect the diffusion of vapors from the stream to the filter surface. One important parameter is residence time of the gases in the filter, which is directly proportional to filter length in a standardized smoking process. The effect of filter length is illustrated in Figure 2 for untreated filters and filters treated with 29% added di(2-methoxyethyl) phthalate. It is evident in this model gas test with acetone vapor that filter length and equivalently residence time considerably affect the removal of this organic vapor. Normal length 20 mm additive filters remove 20 to 25% of the passing acetone vapor, while a very long 50 mm filter removes slightly more than half the vapor presented to it. Smoking tests indicated a similar increasing vapor removal

FIGURE 2

Infra-red measurement of effect of filter length on removal of acetone vapor

with increasing filter length. Because the filtration effect was most pronounced at longer filter lengths, long 50 mm filters were used throughout this work to provide a more complete test of various additives. From consideration of the diffusion process, it is to be expected that the surface area of the filter media and the interfiber separation would also affect the vapor removal. Surprisingly, experimental tests with filters varying two fold in average interfiber separation and two to three fold in fiber surface area did not indicate any marked difference in vapor removal. This suggests that the diffusion process is not a simple matter in the irregular channels of a cigarette filter, but a complex process. As indicated by Figure 2, this complex process appears to be highly dependent on residence time and filter length.

FIGURE 3

Acetone vapor removed by 50 mm filters treated with glyceryl triacetate and di(2-methoxyethyl) phthalate liquid additives

of vapor removal decreases as larger quantities of both additives are applied. As the surface of the filter becomes more completely covered with a film of additive, it is to be expected that further additions would result in less improvement in vapor removal efficiency.

As indicated in Figure 3, the composition of the liquid additive plays a considerable role in determining vapor removal efficiency. The two esters tested show a somewhat different capacity for removing acetone vapor from the gas stream. To test this chemical specificity of vapor removal further, a considerable variety of non-volatile liquids were applied to a 3.9 denier tow filter

TABLE 1

Overall vapor removal efficiency for 10 selected vapor components* for various liquid additives (25–35% added liquid, 50 mm filters of 3.9 denier per filament, 55,000 total denier cellulose acetate tow)

Liquid additive	Overall vapor removal
Glyceryl triacetate**	20%
Ethyl naphthoate	30%
Water	36%
Di(2-methoxyethyl) phthalate**	38%
Tetraethylene glycol dimethyl ether**	42%
Diglycol amine	43%
Polyethylene glycol (m. w. 200)	44%
Triethyl citrate**	44%
Acetyl triethyl citrate	53%
N,N dimethyl caprylamide**	58%

* Isoprene, acetaldehyde, 2-methyl furan and propionaldehyde, methanol, acrolein, benzene, acetone, 2-butanone, toluene and 2,3-butanedione.

** These materials act as bonding agents.

A second parameter of interest is the effect of liquid additive level on vapor removal efficiency. Figure 3 illustrates this for two common acetate bonding and plasticizing agents, di(2-methoxyethyl) phthalate and glyceryl triacetate. These were tested for removal of acetone vapor at a lower concentration than was used in the previous test and at its approximate concentration in cigarette smoke. With this lower concentration of acetone in the gas stream, a lower removal was observed for the 50 mm tips tested. Increasing the additive level of both plasticizing agents resulted in an increase of vapor removal. There is an indication that the rate of improvement

and were subjected to the smoking test procedure. Table 1 summarizes the overall vapor removal efficiencies of these treated 50 mm filters, and Table 2 gives individual removal efficiencies for five selected components of differing chemical properties. In Table 1 it is apparent that the range of liquid additives listed remove quite different overall amounts of the passing vapor phase. Glyceryl triacetate, the common plasticizer triacetin, removes a relatively small amount of the vapor phase while the amide of caprylic acid and dimethyl amine removes approximately 60% of the vapors presented to it. In Table 2 the filtering action of these materials is further specified by listing the individual vapor component retention efficiencies. Several pertinent observations are applicable to these data. The first of these is that a general retention trend, roughly paralleling the

TABLE 2

Percent vapor removal efficiencies for selected components

(same filters as listed in Table 1)

volatility of the tabulated vapor components is apparent in these data. Lower boiling components such as isoprene (b. p. 34°C) and acetaldehyde (b. p. 20°C) are in general less effectively removed than higher boiling components such as toluene (b. p. 111°C). In this respect these filters are similar to charcoal filters in that the more easily condensed components are more completely filtered.

The second and possibly more interesting observation is that con-

siderable chemical selectivity is evident in these data. An example of this is found in the excellent removal of water soluble polar components and lack of removal of toluene by the water-bearing filter. Another example is the excellent removal of toluene, an aromatic hydrocarbon, by ethyl naphthoate which has a degree of similarity in chemical structure. A further example is the capacity of diglycol amine to remove acetaldehyde and methanol quite selectively. This action is not surprising in light of the tendency of amines to interact with aldehydes and alcohols.

Most of the additives listed in Tables 1 and 2 are materials which would be expected to permeate and swell the cellulose acetate substrate of the filter. Half of the listed compounds do this to a sufficient degree to cause a solvation and surface bonding of the acetate fibers, and a sixth material, the relatively effective acetyl triethyl citrate, is found to provide a degree of interfiber bonding at elevated temperatures. This ability to permeate the surface of the acetate fiber substrate suggests a further step in the process of vapor removal. This is that the vapor molecules sorbed on the coated fiber surface are further removed from possible re-entry into the vapor stream by their diffusion away from the gas-liquid additive interface. This action, which can be labelled an absorption, would be enhanced by liquid additives which in themselves permeated or softened the solid fiber. Such a mechanism has been proposed to explain the improved filtering action of plasticized cellulose acetate for phenol and its homologs (11).

To test this absorption hypothesis, a series of filters were prepared with a common liquid additive, triethyl citrate, and different substrates. These ranged from an essentially impervious glass fiber through cellulosic fibers, rayon and cellulose acetate, which are relatively polar, to a non-polar polypropylene fiber. In Table 3, vapor removal efficiency data obtained from smoking tests of these filters are reported. These data tend to confirm the role of absorption in vapor filtration. The impervious glass fiber filter shows a low selectivity for the quite volatile vapors but appreciably adsorbs higher boiling materials such as toluene. The other filters, with the possible exception of the relatively inert rayon, remove appreciably greater quantities of the various gaseous components. The cellulose acetate filter, which is chemically and physically most similar to the rayon filter, removes the largest amounts of those components particularly soluble in it, acetaldehyde, methanol, and acetone. On the other hand, the polypropylene filter appears to have the highest affinity for hydrocarbon vapors with lesser but still appreciable affinity for other organic vapors.

TABLE 3

Vapor removal efficiencies of various fibers treated with triethyl citrate

(44-50% added, 50 mm tips)

Liquid additive	Iso- pre- ne	Acetal- dehyde	Metha- nol	Acetone	Toluene
Glyceryl triacetate	0	4	32	23	23
Ethyl naphthoate	9	4	24	27	73
Water	20	42	53	76	0
Di(2-methoxyethyl) phthalate	10	19	48	39	50
Tetraethylene glycol dimethyl ether	10	17	27	39	57
Diglycol amine	1	63	72	32	43
Polyethylene glycol (200 mw)	13	29	43	46	49
Triethyl citrate	6	25	35	47	68
Acetyl triethyl citrate	22	36	78	52	74
N,N dimethyl caprylamide	14	23	81	45	92

FIBER	Iso- pre- ne	Acetal- dehyde	Metha- nol	Acetone	Toluene
Cellulose acetate	20	33	75	60	79
Polypropylene	30	31	68	54	86
Glass wool	0	3	2	38	72
Rayon	18	20	36	36	76

The data presented in the preceding sections of this paper provide indications of the important factors in the process of vapor filtration. It is first apparent from Figure. 1 that sufficient time must be allowed for the diffusion of vapors from the stream to the surface of the filter fiber. This process seems to require residence times of the order of tenths of seconds rather than microseconds as might be computed by ordinary diffusion calculations. A further complicating factor in the smoke situation is the presence of numerous smoke particles which can also absorb and distill vapors in competition with the filter media. From the operation of charcoal filters, it is predictable that greatly increased filter surface area would reduce these diffusion time requirements, although tests within the range of surface areas available in acetate tow filters indicate little effect of surface. The chemical nature of the surface, as determined by the liquid coating in these experiments, evidently plays a critical role in the removal of vapors. Quite considerable selectivity can be incorporated in these filters by suitable choice of liquid additive. Guidelines for the choice of additive appear to be contained in similar polarity of the additive and the vapor to be removed and in the potential for chemical reaction between the additive and vapor. The degree of selectivity that is achieved with such additives and the overall enhanced vapor removal of liquid additive filters indicate that the sorption of vapors from the gas stream and from deposited smoke particles is very dependent on the nature of the surface.

The final phase of the removal process evidently involves the absorption or diffusion of the captured vapor molecules into the interior of the filter fiber. Although this part of the process plays an important role, it appears to be less critical than the nature of the liquid coating. Differences between fiber substrates have, however, been detected and the effect appears to be dependent on the chemical nature and physical structure of the fiber.

In conclusion, it has been found that the filtering action of fibrous filters can be modified by the addition of considerable quantities of liquids to the fiber surface. These liquid coatings are found to enhance the removal of volatile organic vapors from the smoke stream selectively. The essential parameters of a selectively operating filter are found to be residence time of vapors within the filter and nature of the liquid coating. Diffusion of captured vapors into the fiber plays a secondary role in the removal process. Because of the requirements of filter length and high liquid add on, these filters are of little current practical utility.

SUMMARY

To investigate the ability of fibrous filters to remove volatile smoke components selectively, filters containing quantities of liquid additives on a fibrous substrate were prepared and tested. Using long filter tips, selective filtration of vaporous materials such as isoprene, acetaldehyde, methanol, acetone, and toluene was achieved. It was found that vapor transport to the filter surface and the sorption of vapors by the liquid coating were of great importance in the process. Diffusion of vapors into the substrate fibers was also found to be important, but was less effective in modifying the filtration properties.

ZUSAMMENFASSUNG

Mit dem Ziel, die selektive Wirkung faserigen Filtermaterials auf flüchtige Rauchbestandteile zu prüfen, wurden Acetatfilter mit flüssigen Additiven versetzt und untersucht. Unter Verwendung langer Filtermundstücke konnte eine selektive Filtration dampfförmiger Stoffe wie Isopren, Acetaldehyd, Methanol, Aceton und Toluol festgestellt werden. Der Transport der Dämpfe zur Filteroberfläche und die Sorption der Dämpfe durch den flüssigen Überzug erwiesen sich als besonders wichtig. Auch die Diffusion der Dämpfe in die Filterfasern spielte dabei eine Rolle, trug aber weniger zur Beeinflussung der Filtrationseigenschaften bei.

RÉSUMÉ

Pour étudier la capacité des filtres à fibres à retenir sélectivement les composants volatils de la fumée on a préparé et expérimenté des filtres contenant diverses quantités d'additifs liquides sur substrat fibreux. Avec des bouts-filtres longs on a obtenu la filtration sélective de substances à l'état de vapeurs telles que l'isoprène, l'acétaldéhyde, le méthanol, l'acétone et le toluène. On a trouvé que le transport des vapeurs à la surface du filtre et la sorption des vapeurs par la couche liquide avaient une grande importance dans le processus. On a trouvé que la diffusion des vapeurs dans le substrat fibreux avait aussi de l'importance mais était moins efficace pour la modification des propriétés de filtration.

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