United States Patent

[11] 3,608,564

[72] Inventors **Hiroji Takahashi**
Hiroshima;
Atsushi Saito, Toyama; Kazuo Kuwahara,
Yamaguchi; Katsumi Hayashi, Tokyo;
Takashi Kaneko, Hiroshima; Shigeya
Hayashi, Tokyo; Kenji Okano, Hiroshima,
all of Japan

[21] Appl. No. **825,069**
[22] Filed **May 15, 1969**
[45] Patented **Sept. 28, 1971**

[73] Assignees **Mitsubishi Rayon Co., Ltd.;**
Mitsubishi Acetate Co., Ltd.
Chuo-ku, Tokyo, Japan

[32] Priority **May 15, 1968**
[33] **Japan**
[31] **43/32728**

---

[54] **CIGARETTE FILTER**
22 Claims, No Drawings

[52] **U.S. Cl.** **131/266,**
131/262 A, 131/269
[51] **Int. Cl.** **A24b 15/02,**
A24d 01/06
[50] **Field of Search** 131/266,
269, 267; 260/885

[56] **References Cited**

UNITED STATES PATENTS

2,343,091	2/1944	Smith	260/885 X
2,902,420	9/1959	Norrish	260/885 X
3,004,851	10/1961	Brown	260/885 X
3,083,172	3/1963	Scott et al.	260/885 X
3,098,838	7/1963	Goldberg et al.	260/885 X
3,297,786	1/1967	Horowitz	260/855 X
3,470,883	1/1969	Shepherd et al.	131/10 R
2,077,298	4/1937	Zelger	131/269 UX
2,933,460	4/1960	Richter et al.	131/267 UX
3,148,101	9/1964	Allman et al.	131/266 UX
3,220,960	11/1965	Wichterle et al.	131/269 UX
3,464,423	9/1969	Klein	131/266 X

OTHER REFERENCES

Irwin, T. Hydron New Miracle Plastic With Myriad of Uses Popular Science. Vol. 194, No. 2, February, 1969 p. 92– 95 Pages 93 & 95 cited.

Primary Examiner—Samuel Koren
Assistant Examiner—George M. Yahwak
Attorney—Sughrue, Rothwell, Mion, Zinn & Macpeak

ABSTRACT: Cigarette filters comprising one graft polymer selected from the group consisting of polyvinyl alcohol grafted with at least one monoethylenically unsaturated vinyl monomer and partially saponified polyvinyl alcohol grafted with at least one monoethylenically unsaturated vinyl monomer. A plug comprising a bundle of opened fibers to fit a cigarette carries said polymer.

CIGARETTE FILTER

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a cigarette filter which effectively removes tar and nicotine, and to a method of making the same.

2. Description of the Prior Art

Hitherto, many species of fibrous materials have been used as the raw material for cigarette filters. As an excellent filter produced commercially, there is one comprising a bundle of crimped cellulose acetate fibers as described in U.S. Pat. No. 2,794,239. This filter has a certain degree of filtration capacity for injurious materials, it is easy to form it continuously and quickly in a rod shape and it is possible to use nonvolatile plasticizers such as triacetin, etc. However, it is still necessary to develop a filter having a high filtration ratio, since injurious materials are not completely removed from smoke of the cigarette by the above filter, and the ratio of tar and nicotine removal is not high.

Other methods comprise varying the surface and section of the filter fibers, and using starch or derivatives thereof cellulose derivatives such as cellulose, methyl cellulose, oxycellulose and partially hydrolyzed cellulose, vinyl polymers such as polymethyl methacrylate, polyvinyl acetate and polyvinyl butyral, activated alumina, silica gel, ion exchange resins and activated carbon as the adsorbent. These have a fault of impairing the flavor of tobacco, though the nicotine removal thereof is excellent.

This invention has been completed as the result of many studies about methods for producing a cigarette filter having good tar and nicotine removal which does not injure the flavor of the cigarette at smoking.

SUMMARY OF THE INVENTION

The present invention involves the discovery of an improved cigarette filter formed from at least one graft copolymer selected from the group consisting of polyvinyl alcohol grafted with at least one monoethylenically unsaturated vinyl monomer and partially saponified polyvinyl acetate grafted with at least one monoethylenically unsaturated vinyl monomer.

It is an object of the present invention to provide an improved cigarette filter.

It is a further object of the present invention to provide materials for use in a cigarette filter which provide excellent tar and nicotine removal, and also provide an excellent flavor during smoking.

It is a further object of the present invention to provide a cigarette filter which is capable of yielding a valuable tar and nicotine removal ratio.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to a cigarette filter which is saponified by comprising a graft copolymer composed of polyvinyl alcohol grafted with a copolymerizable vinyl compound and partially saponified polyvinyl acetate grafted with copolymerizable vinyl compound.

The most preferable filter in this invention is one comprising a porous finely divided powder of said graft copolymer having a surface area of 15 to 200 m.²/g. and a 10 to 300 mesh particle size dispersed in a bundle of mechanically crimped cellulose diacetate fibers having a 1.6 to 15 denier monofilament size and from 30,000 to 90,000 total filaments denier.

As the base polymer, polyvinyl alcohol and partially saponified polyvinyl acetate is employed. The degree of polymerization of these polymers are preferably from 300 to 10,000.

The monethylenically unsaturated vinyl monomers grafted to these polymers, which are not restricted, include acrylic acid, methacrylic acid and alkyl esters of these acids, for example, methyl methacrylate, methyl acrylate, ethyl acrylate and butyl acrylate, which have a carbon number from 2 to 18,

acrylamide, acrylonitrile, vinyl chloride, vinylidene chloride, vinyl acetate, ethylene, propylene and styrene. These monomers are used alone or by mixing two or more thereof. Ester-type monomers are most preferred among these monomers, and graft polymers produced therefrom have high affinity for tar and nicotine. Consequently, good filters are obtainable.

The amount of the vinyl monomer grafted to the base polymer is from 10 to 310 weight percent to the polymer. If it is less than 10 weight percent, effective results are not obtained in the resulting graft polymer, and if it is over 310 weight percent, the flavor of the smoke decreases. Further, it is not preferred to graft in an amount of over 310 weight percent because of difficulty in processing. The amount of the branching polymer is preferably from 10 to 310 weight percent to the base polymer.

Since graft polymers in this range have excellent affinity for tar and nicotine and give excellent flavor at smoking, it is possible to produce excellent cigarette filters using said polymers.

As the method of graft polymerization used in this invention, any method may be adopted according to the kinds of vinyl monomers, such as a method using a persulfate, a peroxide, a cerium salt or an azobisisobutylonitrile as the catalyst, or methods utilizing radioactive rays, etc. Further, the polymerization may be carried out either in a homogenous system or in a heterogeneous system. In other words, the polymerization process per se is not critical.

These polymers have good absorbing capacity for the ingredients which afford a bitter taste and a stimulative smell in the smoke of tobacco, such as phenols and aldehydes, but have a suitable degree of adsorbing capacity with respect to ingredients which lend good flavor, such as water and organic acids. Accordingly, cigarettes using the filter of this invention do not have a stimulative smell, a bitter taste or a lack of flavor, because these fibers decrease tar and nicotine in cigarette smoke to give a pleasant taste to the smoke. Furthermore, it is possible to vary the ratio of removal of tar and nicotine by changing the species and the ratio of vinyl monomers. Accordingly, it is possible to produce cigarette filters corresponding to the kind of tobacco and the kind of taste desired.

Though there are many shapes of the graft polymers which can be used in the cigarette filter, a finely divided powder is most preferable.

The finely divided powder has a 10 to 300 mesh, preferably from 60 to 80 mesh, particle size, and most preferably a 15 to 200 m.²/g. surface area. It becomes a porous finely divided powder. In this case, the specific gravity thereof is from 1.1 to 0.2.

The finely divided powder can be produced by the following methods. (1) A polymer slurry which is prepared as a solution or dispersion of graft polymer gelatinized in poor solvent, water or by salting out gradually, is separated by precipitation, dried, powdered and screened to arrange the particle size within the range described above. (2) A solution or dispersion containing the graft polymer is frozen at less than −20° C., and then solvent is removed under a reduced pressure of from 18 mm. Hg to 1.2×10^{13} mm. Hg After drying, the polymer is powdered. (3) A solution or dispersion containing the graft polymer is dried by spraying into a dry heating stream at 60°–130° C. or by spraying at from 40° to 110° C. under from 260 to 58 mm. Hg., and then the polymer is powdered.

The resulting porous finely divided powder is dispersed in a raw material of the filter, for example, an opened fiber bundle, and then the fiber bundle is formed into a rod shape and finally into the filter tip shape. The method for producing the filter by adding the powder into the fiber bundle is not restricted. The easiest method comprises uniformly dispersing the powder in an opened tow by a disperser as used in the step of making common filter plugs, such as by rolling up a paper to a 7.9 mm. diameter with a cigarette paper rolling machine to produce a filter plug, and cutting such a plug to a 17 mm. length to make filter tips.

The most preferred filter in this invention is that comprising from 5 to 80 percent of a porous finely divided powder (consisting of the graft polymer as described above based on the weight of fibers) dispersed in a fiber bundle of mechanically crimped cellulose diacetate having a 1.6 to 8 denier monofilament size, a 30,000 to 90,000 total filament denier, and with crimps of from 5 to 30/inch.

The finely divided powder of the graft polymer prepared by grafting the monoethylenically unsaturated vinyl monomers to the polyvinyl alcohol and the partially saponified polyvinyl acetate does not have a large adsorbing capacity for water, and is comparatively hard before smoking. Further, it does not become sodden by moisture in the mouth or the tobacco and have the adsorption resistance increase by dissolution of polyvinyl alcohol by the moisture. Furthermore, since the finely divided powder has a suitable hydrophobic property, it has the characteristic that the smoke of the tobacco does not dry excessively. Moreover, since the removal of perfume, often added during preparation of the tobacco, is small when compared with the removal upon the use of polyvinyl alcohol, the smoking taste of the tobacco is not injured.

In producing the fiber as described above, an adhesive consisting of a solution or dispersion containing more than 20 weight percent of a plasticizer such as triacetin, the acetate of ethyleneglycol, the acetate of polyethylene glycol and methylethyl ether, etc., or vinyl acetate, may be sprayed in an amount of from 5 to 18 weight percent (to the fiber tow) in order to bind the fibers to themselves, as well as to bind the finely divided powder and fibers. If desired, other additives or adsorbents for injurious materials may be used together therewith.

Thought it is most preferable to use cellulose diacetate as the fiber (as described above), any fiber, for example polypropylene fiber or viscose fiber, which is known as suitable for cigarette filter fibers, may be used.

Besides the filter described above, a filter which is produced by spraying a solution or dispersion of the graft polymer onto the filter tow to cause the graft polymer to adhere to the surface of fibers, removing solvent and forming said tow by rolling it up with a paper is included in this invention.

Further, filters in which a finely divided powder is contained as associated matter are included in this invention. For example, there are filter tips in which a finely divided powder is contained therein as capsules, and filter tips in which said powder is sandwiched between fiber filters.

A polymer prepared by grafting methyl methacrylate to polyvinyl alcohol and partially saponified polyvinyl acetate is quite soluble in acetone, dimethylsulfoxide (DMSO) and dimethylformamide (DMF).

However, from the viewpoint of its toxic character and the ease of removal of the solvent, DMSO and DMF are not suitable as the solvent of the graft polymer, and acetone is preferably used.

Solvents for polymers grafted by vinyl monomers besides methyl methacrylate are as follows.

Methyl acrylate:	Ethyl acetate, DMSO and DMF.
Ethyl acrylate:	Toluene, DMSO and DMF.
Butyl acrylate:	Toluene, DMSO and DMF.
Acrylamide:	DMF.
Acrylonitrile:	DMSO and DMF.

However, employable solvents are restricted by the above-mentioned reasons, i.e., toxicity and ease of removal.

When a suitable solvent is not present, the graft polymer is dispersed in a nonsolvent together with a surface active agent to produce a homogeneous emulsion, which is then sprayed onto the fiber bundle.

Before turning to the examples, the various methods used therein will be explained.

The "standard" tobacco described in this specification was a side-cut (both sides) cigarette made by the Nippon Monopoly Corporation, from which the acetate filter tips had been removed. Cigarettes having a 78±2 mm.H_2O gas permeation resistance were selected for use.

Gas permeation resistance	Flux 17.5ml./sec.	
Conditions of smoking	Smoking device:	definite flux type
	Smoking time:	2 sec/round
	Smoking interval:	58 sec
	Smoking flux:	17.5 ml/sec
	Smoking round:	8/cigarette
Method for collecting smoke:	Cambridge Filter CM-113 (10% aqueous sodium hydroxide solution for phenolic compounds)	
Number of cigarettes smoked		20
Smoked length		50 mm
Method for analyzing tar		Gravimetric
Method for analyzing nicotine (whose alkaloid)		Alkali steam distillation and ultraviolet ray absorption
Method for analyzing phenolic compounds		Spectrometric method with nitrosophenol

$$\text{Filtration ratio} = \frac{A}{A+B} \times 100$$

A: Amount removed in filter tip

B: Amount removed in Cambridge filter (amount removed in 10% sodium hydroxide solution, in compounds)

The method for measuring the surface area of the porous, finely divided powder used in this invention was the B.E.T. method. Namely, an inert gas is adsorbed in a finely divided powder at near its boiling point. From a graph in which adsorbed amounts of gas are plotted, the amount of the gas necessary to form a monomolecular layer on the surface of the solid is determined, and the relative surface area is determined. This method is explained in detail in the following references.

S. Brunauer, P. H. Emmet, and E. Teller: J. Am. Chem. Soc. 60, p. 309. (1938), and F. M. Nelsen and F. T. Eggertsen: Anal. Chem. 30, p. 1387, (1958).

The tobacco used for determination was conditioned at 25° C., and 60 percent RH for over 48 hours.

EXAMPLE 1

100 parts of partially saponified polyvinyl alcohol having an 8,000 average degree of polymerization and a 92 percent saponification value was dissolved completely in 1,600 parts of boiled distilled water at 85° C. in a nitrogen stream, and then 2.5 parts of the cerium salt of ammonium sulfate, 230 parts of methyl methacrylate, and 2.0 parts of conc. nitric acid (concentration 60–62 percent) were added thereto. The graft polymerization took place at 60° C. for 4 hours (degree of grafting was 135 weight percent). After the reaction was over, the polymerization solution was gradually poured into about a 10-fold amount of methanol with vigorous stirring. The resulting precipitate was washed, filtered and dried, and then powdered to give a finely divided powder having a 60–80 mesh particle size. This powder had a 14.2 m.^{2}/g. surface area average.

A tow of cellulose diacetate filaments mechanically crimped having a 4 denier monofilament size and a 55,000 total filament denier was opened. After spraying triacetin in an amount of 6.7 weight percent to the tow, the finely divided powder described above (consisting of polyvinyl alcohol grafted with methyl methacrylate) was dispersed in an amount of 29.8 weight percent to the tow by a disperser together with a gas stream at from 28 to 30 cm./sec. flux. The tow was then rolled up to a 7.9 mm. diameter using a paper by means of a cigarette plug making machine to produce a filter plug.

The plug was cut to a 17 mm. length to produce tips. A tip was then put onto an end of the standard cigarette by a cellophane tape having a 12 mm. width so as to keep it in close contact with the cutting surface. The properties of the resulting filter are shown in table 1, in comparison with those of a filter which does not contain a finely divided graft polymer powder.

The filter of this invention not only provides good removal of tar and nicotine in tobacco smoke, but good removal of phenolic compounds (stimulative ingredient) and gives an excellent smoking flavor to smokers.

TABLE 1

	Gas permeation resistance (mm. H_2O)	Percent: Tar removing ratio	Nicotine removing ratio	Phenolic compound removing ratio
This invention	55	49	37	80
Comparative example	49	40	30	64

EXAMPLE 2

100 parts of partially saponified polyvinyl alcohol having an 87 percent saponification value, 35 parts of acrylamide, 180 parts of purified styrene and 2,500 parts of water were mixed under a nitrogen stream. By adding 3.8 parts of persulfate, emulsion polymerization was carried out. The ratio of grafting was 180 percent. After 5 hours, the reaction product was frozen with dry ice and dried under reduced pressure at 1.3 $\times 10^{11}$ mm. Hg The resulting porous material was powdered, and particles having a 80 to 110 mesh size were selected therefrom. The resulting graft copolymer had an approximately 63 m.^{2}/g. surface area, measured by the B.E.T. method.

A tow of cellulose diacetate filaments mechanically crimped having 4 denier monofilaments and a 55,000 total filaments denier was opened. After spraying triacetin in an amount of 6.7 percent based on the weight of the tow, the finely divided powder described above was dispersed in the amount of 32.5 weight percent onto the tow by an electromagnetic vibrator. The tow was then rolled upon a cigarette plug making machine and sufficiently dried. After being plasticized, a plug having a 7.9 mm. diameter was obtained.

The resulting plug was cut into a 17 mm. length to produce tips. By selecting a tip having a definite gas-permeation resistance, the characteristics of the filter were determined. The results are shown in table 2.

TABLE 2

	Gas permeation resistance (mm. H_2O)	Percent: Tar removing ratio	Nicotine removing ratio	Phenolic compound removing ratio
This invention	57	64	47	89
Comparative example	49	40	30	64

EXAMPLE 3

100 parts of partially saponified polyvinyl alcohol having a 6,300 average degree of polymerization and a 64 percent saponification value, 35 parts of acrylamide and 84 parts of methyl methacrylate were mixed with 1,200 parts of distilled water. By the addition of 4.2 parts of persulfate, emulsion polymerization was carried out. The grafting ratio was 63 percent.

The reaction product was force-sprayed into a heating stream at 128° C. to form a finely divided powder. From this finely divided powder, particles of a 60 to 90 mesh size were selected. The surface area of the resulting finely divided powder was approximately 28 m.^{2}/g., measured by the B.E.T. method.

A tow of mechanically crimped polypropylene filaments having a 9.5 denier monofilament and an 82,000 denier total filament size was sufficiently opened. After spraying the tow with a 5 percent toluene solution of 4.2 weight percent of ethylene-vinyl acetate copolymer (72:28) to the tow, the finely divided powder of the graft copolymer described above was dispersed in the amount of 28 weight percent, to the tow.

The tow containing the finely divided powder was treated by a cigarette plug making machine to produce a filter plug having a 7.9 mm. diameter, which was then cut to 102±0.2 mm. By further cutting, filter tips having a 17 mm. length were obtained.

The properties of the resulting filter are shown in table 3, together with a filter composed of the plain prior art polypropylene fibers.

TABLE 3

	Gas permeation resistance (mm. H_2O)	Percent: Tar removing ratio	Nicotine removing ratio	Phenolic compound removing ratio
This invention	58	48	36	72
Comparative example	53	31	27	42

EXAMPLE 4

A graft polymer was produced by mixing 100 parts of partially saponified polyvinyl alcohol which had a 1,750 average degree of polymerization and an 85 percent saponification value, 30 parts of methyl methacrylate and 150 parts of methacrylonitrile in water, and then carrying out emulsion polymerization. Into the system containing the polymer solution was added 95 parts of activated clay. The mixture was frozen at −63° C. and dried under 1 mm. Hg.

The graft polymer obtained was powdered into 60 to 80 mesh size by a mill. The finely divided powder had a 92 m.^{2}/g. surface area.

A tow consisting of mechanically crimped polypropylene filaments having a 9.5 denier monofilament size and an 80,000 total filament size was opened by compressed air. Then a toluene solution of 4.2 weight percent (to the tow) of ethylene-vinyl acetate copolymer (72:28) was sprayed onto the tow. Then the finely divided powder described above was added to the tow in an amount of 31.1 weight percent by a disperser. The tow containing the finely divided powder was treated by a cigarette plug making machine to produce a filter plug having a 7.9 mm. diameter, which was then cut to 102±0.2 mm. By further cutting, filter tips having a 17 mm. length were obtained.

The properties of this filter tip are shown in table 4, in comparison with those of a filter which does not contain the finely divided powder of this invention.

TABLE 4

	Air permeation resistance (mm. H_2O)	Percent: Tar removing ratio	Nicotine removing ratio	Phenolic compound removing ratio
This invention	57	57	43	76
Comparative example	51	29	25	40

EXAMPLE 5

100 parts of partially saponified polyvinyl alcohol having a 500 degree of polymerization, a 60 percent saponification value and 100 parts of acrylamide were mixed in water. Graft polymerization was carried out by adding ceric ammonium nitrate at 70° C. for 3 hours. The grafting ratio of the resulting polymer was 34 weight percent.

The graft polymer was dissolved in toluene to produce a solution having a 2 weight percent concentration. Mechanically crimped cellulose diacetate filaments having a 4 denier monofilament size and a 55,000 denier total filament size were sufficiently opened, and then the toluene solution containing the graft polymer was sprayed thereon by a centrifugal device for adding a plasticizer. The graft polymer was contained in the tow at an amount of 10 weight percent. Triacetin was then sprayed (6 weight percent) onto the tow by a centrifugal plasticizer applicator. The tow was treated by a cigarette plug making machine to produce a plug having a 7.8 mm. diameter, which was then cut to 102±0.2 mm. After further cutting to 17 mm., filter tips were obtained.

TABLE 5

	Gas permeation resistance (mm. H_2O)	Percent		
		Tar removing ratio	Nicotine removing ratio	Phenolic compound removing ratio
This invention	60	51	42	75
Comparative example	49	40	28	64

properties of the filter tip are shown in the table 5, in comparison with those of a filter produced by the same procedure but without adding a toluene solution of the graft polymer of this invention.

We claim:

1. In a cigarette filter comprising a plug made from a bundle of opened fibers, the improvement which comprises said fibers having dispersed thereon a porous, finely divided, substantially hydrophobic graft polymer selected from the group consisting of polyvinyl alcohol grafted with at least one monoethylenically unsaturated vinyl monomer and partially saponified polyvinyl alcohol grafted with at least one monoethylenically unsaturated vinyl monomer.

2. Cigarette filters of claim 1 wherein said partially saponified polyvinyl alcohol has a saponification value ranging from about 60 to about 92 percent.

3. Cigarette filters of claim 1 wherein said grafted polymer has a polymerization degree of from 300 to 10,000.

4. Cigarette filters of claim 1 wherein at least one of said vinyl monomers is a compound selected from the group consisting of lower alkyl esters of acrylic acid and lower alkyl esters of methacrylic acid.

5. Cigarette filters of claim 4 wherein said lower alkyl ester of acrylic acid is a compound selected from the group consisting of methyl acrylate, ethyl acrylate and butyl acrylate.

6. Cigarette filters of claim 4 wherein said lower alkyl ester of methacrylic acid is methyl methacrylate.

7. Cigarette filters of claim 1 wherein the grafting ratio ranges from about 10 to about 310 percent by weight of the polymer to be grafted.

8. Cigarette filters of claim 1 wherein said grafted polymer is a finely divided powder having a particle size ranging from about 10 to about 300 mesh.

9. Cigarette filters of claim 8 wherein said grafted polymer is a finely divided powder having a particle size of from about 60 to about 80 mesh.

10. Cigarette filters of claim 8 wherein said finely divided powder has a surface area of from about 15 to about 200 $m.^2/g.$

11. Cigarette filters of claim 8 wherein said finely divided powder is porous and has a specific gravity of from about 0.2 to about 1.1.

12. Cigarette filters of claim 8 wherein said plug is a fiber tow.

13. Cigarette filters of claim 8 wherein the weight of said finely divided powder ranges from about 5 to about 80 percent based on the weight of said plug.

14. Cigarette filters of claim 1 wherein said plug comprises a crimped fiber bundle having a monofilament size ranging from about 1.6 to about 15 denier and from about 30,000 to about 90,000 total filament denier.

15. Cigarette filters of claim 14 wherein said fibers have crimps of from about 5 to 30/inch.

16. Cigarette filters of claim 14 wherein said fibers are celluloe diacetate fibers.

17. Cigarette filters of claim 14 wherein said fibers are polypropylene fibers.

18. Cigarette filters of claim 14 wherein said fibers are viscose fibers.

19. Cigarette filters of claim 1 wherein said plug comprises fibers treated with an adhesive consisting of a solution or dispersion containing more than 20 percent by weight of a plasticizer.

20. Cigarette filters of claim 19 wherein said fibers are sprayed with said adhesive in an amount of from 5 to 18 percent by weight of said fibers.

21. Cigarette filters of claim 19 wherein said plasticizer is a compound selected from the group consisting of triacetin, ethylene glycol acetate, polyethylene glycol acetate, methyl ethyl ether, and vinyl acetate.

22. Cigarette filters of claim 14 wherein the monofilament size of the fiber bundle ranges from 1.6–8.0 denier.