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(54) Cellulose ester fibrillar material having additives imbedded on a surface thereof.

(57) Cellulose ester fibrillar material having additives imbedded in or impregnated upon a surface of said fibrillar material is disclosed herein. The method comprises the steps of: providing a polymer solution or "dope", coagulation liquid, and additive; mixing the polymer solution and coagulation liquid within the attenuation zone of a nozzle; adding the additive to the mixture within the attenuation zone of the nozzle; and thereby forming the fibrillar material.

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Field of the Invention

Cellulose ester fibrillar material, wherein additives are imbedded in or impregnated on the surface of the fibrillar material in such a manner as not to adversely impact the beneficial affects of those additives, and the method of making the same are disclosed herein.

Background of the Invention

Cellulose ester fibrillar material is known (see U. S. Patent Nos. 3,842,007 and 4,192,838). Cellulose acetate fibrillar material is commercially available from the Hoechst Celanese Corporation of Charlotte, NC under the tradename of "Cellulose Acetate Fibrets". The chemical process by which these materials are made is also well known. Ibid. Moreover, several methods of manufacturing this fibrillar material have been proposed (see in U. S. Patent Nos. 3,842,007; 4,017,862; and 4,192,838).

Cellulose ester fibrillar material has application in a wide variety of end uses. Such end uses include, but are not limited to, filtration and nonwovens. Within filtration applications, the fibrils can be used, alone, as a filter aid (see in U. S. Patent No. 3,842,007) or as a component in filter sheets (see U. S. Patent Nos. 4,283,186 and 5,002,964) or as a component in filter disks. With regard to the nonwoven applications, the fibrils can be used to bind components of the nonwoven (see in U. S. Patent No. 4,192,838).

Many of the applications for such fibrils rely, at least in part, upon their unusually high surface area which results from their very fine, fibrillar structure. Fibrets typically have a surface area of over 5 square meters per gram. Individual fibrets have a length of between 0.1 to 1,000 microns and a diameter ranging from 0.2 to 0.6 microns.

With specific regard to filtration applications, there is often a need to increase the affinity of the cellulose ester fibrillar material for a particular material or "target material" to be removed from a media. Additives with various properties can be used to influence the affinity of the fibril for such target materials. However, the incorporation of such additives into the cellulose ester fibrillar material is not straight forward because, during incorporation, the additive may lose its affinity, i.e., it may be encapsulated by the cellulose ester, for the target material or may not be securely affixed to the fibrillar material.

Various schemes have been devised or suggested to combine the additive and the fibril. One scheme is the mixture of the additive into the cellulose ester precursor solution prior to fibril formation. Addition of an opacifier to fibrets is known. See U. S. Patent No. 4,460,647. This scheme is limited for filtration applications because the additive is embedded within the fibril and is blinded by the cellulose ester, so that the additive looses its efficacy for enhancing the fibril's affinity for the specified target material. An alternate scheme is the combination of the additive and the fibril after fibril manufacture. This scheme is limited because the additive does not always adhere to the surface of the fibril, thus the additive can be dusted off or washed away from the fibril during use. Finally, an adhesive could be used to prevent the loss of the additive (for example, see in U. S. Patent Nos. 4,007,114 and 4,647,324), but the use of the adhesive can be detrimental in two ways. First, the adhesive could blind the additive and thus dull its affinity for the target material. Second, the adhesive could bind fibrils together whereby the high surface area of the fibrils is lost.

In dissimilar, non-related filter medias, such as melt-blown nonwovens (see, for example, in U. S. Patent No. 4,797,318), particles are blown against microfiber materials after formation but before solidification. The particles are then attached to the surface of the melt-blown microfibers forming the nonwoven. This material does not suggest the invention disclosed herein because the microfibers must be melt processable, i.e. thermoplastic. The cellulose esters used in this invention are not melt processable, instead, they are solution processable.

Accordingly, there is a need for a method by which additives can be disposed upon the surface of a cellulose ester fibril in such a way that the affinity of the additive is not reduced, the high surface area characteristic of the fibril is retained and the additive is secured to the surface of the fibril.

Summary of the Invention

Cellulose ester fibrillar material having additives imbedded in or impregnated upon a surface of said fibrillar material is disclosed herein. The method comprises the steps of: providing a polymer solution or "dope", coagulation liquid, and additive; mixing the polymer solution and coagulation liquid within the attenuation zone of a nozzle; adding the additive to the mixture within the attenuation zone of the nozzle; and thereby forming the fibrillar material.

Description of the Drawing

For the purpose of illustrating the invention, there is shown in the drawings a form which is presently preferred; it being understood, however, that this invention is not limited to the precise arrangement and instrumentality shown.

Figure 1 is a schematic representation of a process wherein cellulose ester fibrillar material is made with additives disposed on the surface of the fibrillar material.

Figure 2 is a cross sectional representation of an attenuation nozzle used in one embodiment of the instant invention.

Figure 3 is a cross sectional representation of the attenuation nozzle used in an alternate embodiment of the instant invention.

Figure 4 is a photo micrograph (x500) of cellulose acetate fibrils with an additive (bentonite) that is made according to the instant invention.

Detailed Description of the Invention

The manufacture of cellulose ester fibrillar material, as set forth above, is well known. Generally, the manufacture of cellulose ester fibrils comprises the production of solvated cellulose ester material (also referred to as a "polymer solution"), commonly referred to as a "dope". This dope is then injected through an attenuation nozzle, under conditions of high shear, where it is mixed with a coagulating liquid. In this nozzle, the cellulose ester solvent is leached from the cellulose ester whereby the fibrils are formed. Thereafter, the fibrils undergo a series of dewatering, homogenizing and drying steps. The instant invention may be used with any of the known dope and/or coagulation liquid formulations or downstreaming dewatering, homogenizing and drying steps.

The term "cellulose ester" refers to, but is not limited to, cellulose acetate, cellulose triacetate, cellulose acetate butyrate, benzyl cellulose, or mixtures thereof. The term "fibrillar material" or "fibril" refers to, but is not limited to, microfibers having surface areas in excess of 5.0 square meters per gram, length less than 1000 microns, and diameters from about 0.2 to 90 microns. Preferably, cellulose ester fibrils have a surface area of about 20 square meters per gram, lengths of about 20 - 200 microns, and diameters of about 0.5 - 5 microns. The term "additive" refers to, but is not limited to, any material that has a particular affinity for another material or that has a special ability to entrap or absorb or adsorb another material (for example, bentonite, activated carbon, zeolites, etc.). The term "dope" or "polymer solution" or "cellulose ester solution" refers to, but is not limited to, a 5-15% solution of cellulose ester (based upon the weight of the cellulose ester). The solvent component of the dope or cellulose ester solution may comprise a solvent for the cellulose ester, alone, or a mixture of the solvent for the cellulose ester (comprising 80%-98% by weight) and a nonsolvent for cellulose ester (comprising 2-20% by weight) which is miscible in the solvent for the cellulose ester. The term "coagulation liquid" refers to, but is not limited to, a mixture consisting essentially of the nonsolvent for the cellulose ester, but it may also include up to 10% by weight of the solvent. In a preferred embodiment of the invention, the cellulose ester is cellulose acetate, the solvent is acetone, and the nonsolvent is water.

It has been determined that additives can be affixed to the surface of a fibril without the loss of the additives' affinity for a particular target material, the loss of the high surface area of the fibril, by injecting the additive, typically in the form of a slurry, into the attenuation nozzle during fibril formation.

Referring to Figure 1, there is shown schematic representation of a cellulose ester manufacturing scheme 10. Dope is delivered to an attenuation nozzle 30 from dope supply 12 via an optional metering pump 16 and dope heater 14. Coagulating liquid is delivered to nozzle 30 from supply 18 via high pressure pump 20. Additive is delivered into nozzle 30 from additive tank 22 via metering pump 24. Alternatively, additive may also be metered into the coagulation liquid and carried to nozzle 30 (as illustrated in phantom). Further details regarding attenuation nozzle 30 are set forth hereinafter. Within nozzle 30, dope, coagulation liquid and additive are brought together, under high shear condition, in such a manner that as the coagulation liquid leaches the solvent from the cellulose ester, thereby forming the fibrils, and the additive is disposed upon the surface of the fibril. Thus, a fibril having additive at the surface of the fibril is formed. The thus-formed fibrils are deposited upon a screen 26 and excess solvent from the dope and coagulation liquid is collected in drum 28. As will be understood by those of ordinary skill in the art, the dewatering, homogenizing and drying steps set forth in in U. S. Patent Nos. 3,961,007 and 4,047,862 and in U. S. Application Serial Nos. 07/672,082 filed December 14, 1990 and 07/627,279 filed December 14, 1990, all of which are incorporated herein by reference, could be substituted for the screen and drum collection system.

Referring to Figure 2 there is shown attenuation nozzle 30 of the instant invention. Nozzle 30 comprises an inlet 32 for dope and inlet 34 for coagulation liquid and a capillary 40 through valve stem 42. Additive is injected into an attenuation zone 38 through capillary 40. Inlet 32 for dope is in fluid communication with an annular cavity 44 which opens into attenuation zone 38. Coagulation liquid inlet 34 is in fluid communication with an annular conduit 46 which exits into attenuation zone 38. Within attenuation zone 38, coagulation liquid, dope and additive are intimately mixed in such a way that the additive is disposed upon the exterior surface of the fibret so that the additive's affinity for a particular target material is not diminished.

In Figure 3, nozzle 30' is shown in use of an alternate process. Nozzle 30' is essentially the same of nozzle 30 with the exception that additive can be introduced into the nozzle via the coagulation inlet 34' as well as capillary 40'. In this nozzle 30', additive is disposed upon the surface of the fibret in attenuation zone 38' so that the additive's affinity for a particular target material is not diminished.

In Figure 4, there is shown cellulose ester fibrillar material made in accordance with the foregoing description. The fibrils are the rope-like strands seen throughout the photomicrograph. The additives (bentonite) are seen as the granular material on the surface of the fibrils.

To more fully understand the operation of the instant invention, refer to following Example.

EXAMPLE

A 0.03 inch capillary was drilled through the needle valve stem of a standard attenuation nozzle (See in U. S. Patent No. 4,192,838). The capillary was attached through a 0.25 inch hose to a Cole Parmer Diaphragm Pump (80 to 800 ml/min, 50 psi max. pressure, set at 40% of full scale). 2.5 percent by weight Bentonite was dispersed in acetone in a reservoir and continuously stirred to prevent the particulate from settling to the bottom.

Heated dope was supplied to the fibret nozzle from the preheater heated at a temperature of 60 °C and a Zenith 58 pump speed of 40 rpm. Precipitation water was pumped through the system from a 40 gallon hot water heater set at 170 degrees F and a pressure of 185 psi. Fibrils were collected on a screen support over a 55 gallon drum. Solvent passed through the screen was collected in the drum. After startup with no additive, additive was injected into the dope stream through the capillary in the needle valve stem. Fibril formation was not interrupted by this event.

For comparison, Bentonite was blended directly into a dope and extruded into fibril form. The following zeta potential values were obtained by measuring streaming potentials with a Zeta Data instrument manufactured by Paper Chemistry Laboratory, Inc. of Carmel, NY.

Sample	Zeta Potential
Bentonite Slurry	-53 mV
CA Fibrets	-12 mV
Bentonite added to CA Dope	-27 mV
Bentonite injected per instant invention	-63 mV

The present invention may be embodied in other specific forms without departing from the spirit or essential attributes thereof and, accordingly, reference should be made to the appended claims rather than to the foregoing specification, as indicating the scope of the invention.

Claims

1. A method for the manufacture of cellulose ester fibrillar material, said material having additives imbedded or impregnated upon a surface of said material, said method comprises the steps of:
providing a dope;
providing a coagulation liquid;
providing a nozzle having an attenuation zone;
providing an additive;
mixing, within said attenuation zone of said nozzle, said dope and said coagulation liquid;
adding said additive to said attenuation zone while mixing of said dope and coagulation liquid; and thereby forming the cellulose ester fibrillar material.

2. The method according to claim 1 further comprising:
providing said nozzle including a coagulation inlet, a dope inlet; and

adding said additive via a capillary into said attenuation zone.

3. The method according to claim 1 further comprising:
providing said nozzle including a coagulation inlet, a dope inlet; and
adding said additive via a capillary into said attenuation zone and via said coagulation inlet.

4. A fibril comprises:
a microfiber having a surface area in excess of about 5.0 square meters per gram, a length of less than about 1000 microns, and diameters ranging from about 0.2 to about 90 microns;
said microfiber being made of cellulose ester; and
an additive being imbedded or impregnated on a surface of said microfiber.

5. The fibril according to claim 4 wherein said cellulose ester is selected from the group consisting of cellulose acetate, cellulose triacetate, cellulose acetate butyrate, benzyl cellulose and mixtures thereof.

6. The fibril according to claim 4 wherein said microfiber having a surface area of about 20 square meters per gram, lengths ranging from about 20 to about 200 microns, and diameters ranging from about 0.5 to about 50 microns.

7. The fibril according to claim 4 wherein said additives are selected from the group consisting of bentonite, activated carbon, zeolites and mixtures thereof.

FIG. 1

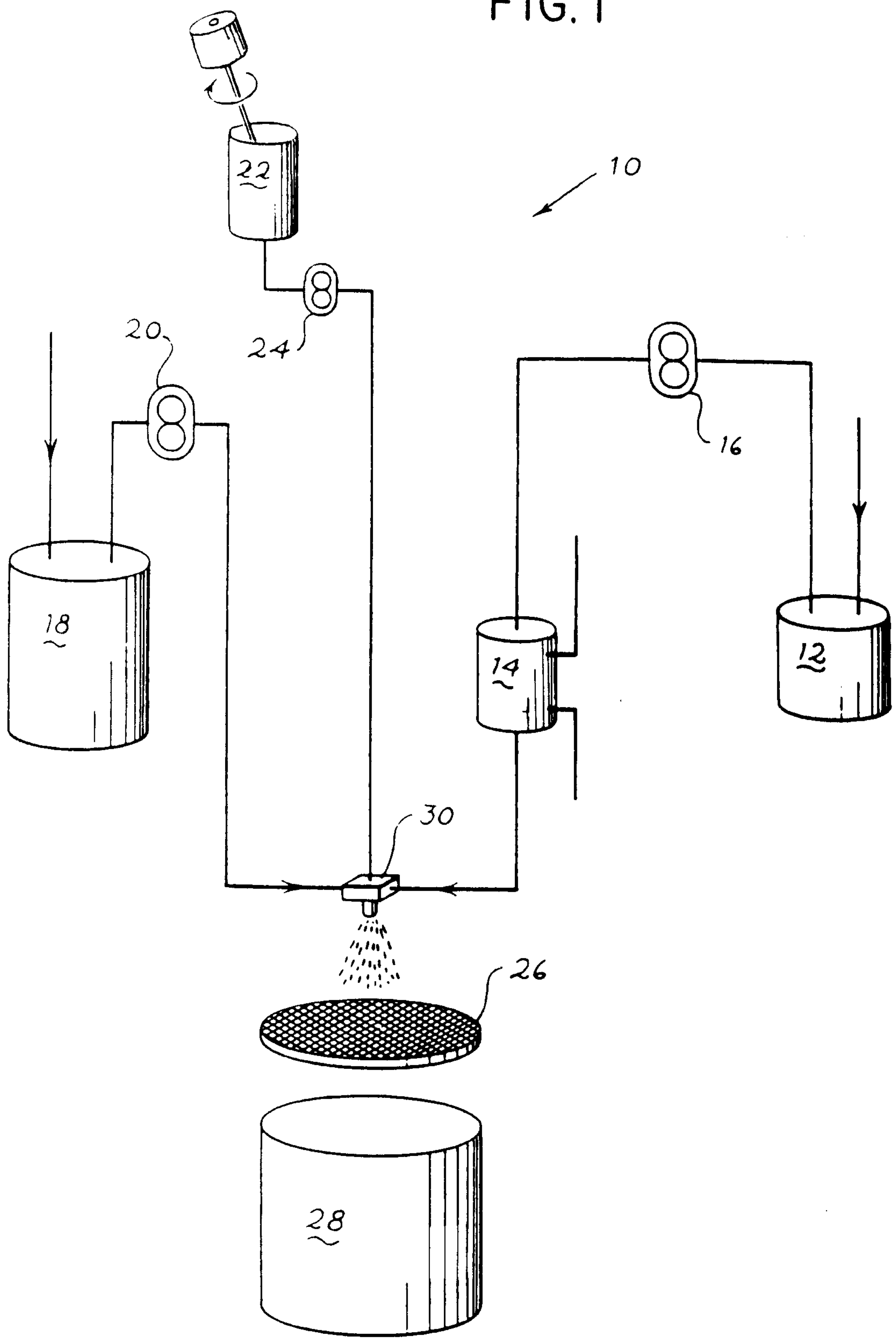

FIG. 2

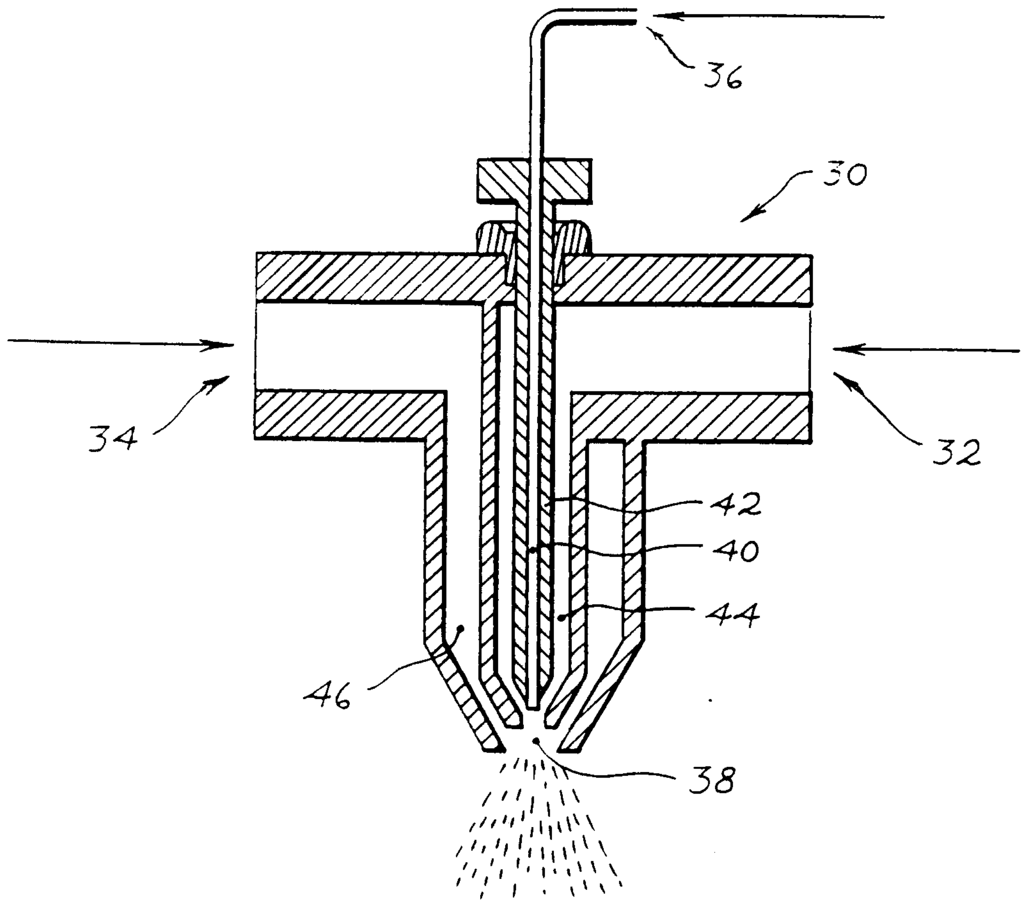

FIG. 3

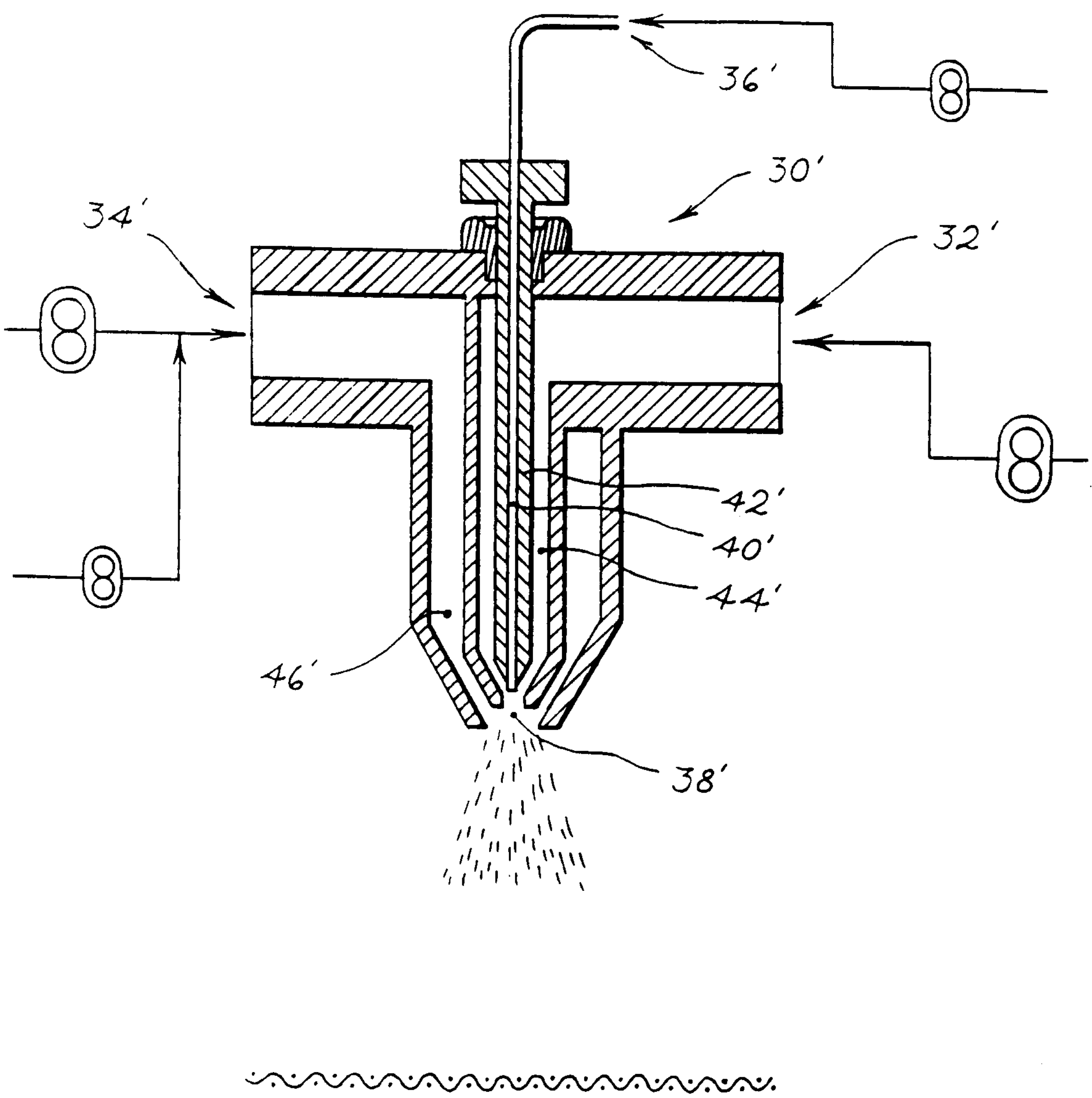

FIG 4