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(54) Title: ULTRAPOROUS AND MICROPOROUS MEMBRANES AND METHOD OF MAKING MEMBRANES

**(57) Abstract**

Ultraporous and microporous polymer membranes cast from metastable dispersions are significantly improved by limiting the time of environmental exposure to less than about 0.5, preferably less than 0.25 seconds, between casting and quenching, and reducing the casting temperatures about 10 to about 20 °C lower than the usual prior art values. The resulting membranes have far less debris entrained in the membrane, far more consistent and uniform pore sizes, a substantially greater number of skin pores, and greatly increased flow rates for any given pore diameter.

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**ULTRAPOROUS AND MICROPOROUS MEMBRANES
AND METHOD OF MAKING MEMBRANES**

BACKGROUND OF THE INVENTION

1. Technical Field of the Invention

5 The present invention relates to ultraporous and microporous membranes which are useful in materials separations, by filtration, dialysis, and the like, and as supports and containment media for materials, and related uses. In particular, it relates to highly asymmetric, integral membranes with a skin and a porous sub-structure or support region.

2. Description of the Prior Art

15 A wide diversity of polymer membranes are known, and have attained wide applicability in diverse uses. Such membranes are characterized by a variety of properties and characteristics, and the selection of a membranes for a particular use is generally a function of the properties required or desired.

20 The most characteristic property of concern for most applications is the effective controlling pore diameter, which defines what materials may pass through the membrane, and which are retained. Ultraporous membranes are generally those with an effective controlling pore diameter of less than about 0.050 micrometers (or sometimes considered to be less than about 0.025 micrometers), down to as 0.005 micrometers, which is the realm of the size of a molecule of, for example, simple sugars and the like. Microporous membranes are those with effective limiting pore diameters of greater than ultraporous, normally greater than about 0.050 micrometers, up to about 1 micrometer, or occasionally more.

35 As used in the present application, the term "pore diameter" is employed to represent the span across skin pores or controlling pores of a membrane. It is not intended to suggest that all pores are circular and, indeed, most are not, as those of ordinary skill in the art will understand and as FIG. 2 illustrates.

Smaller pore membranes extend into the reverse osmosis region and below that into the gas separation region. Reverse osmosis membranes are used for ionic separations, under high applied pressure differentials, sufficient to overcome osmotic pressure, and are sometimes said to be dependent on a mechanism which is often characterized as intermolecular dissolution. Such membranes have a dense, non-porous surface skin, and do not function by effects dependent on seive-like characteristics. As a distinguishing characteristic, reverse osmosis is, in material part, dependent on the osmolarity of a solution as a determinant of the separatory characteristics of the reverse osmosis operation, while ultraporous and microporous membranes pass or retain materials predominantly on the basis of their size, at applied pressure differential which are commonly far less, often an order of magnitude less, than reverse osmosis operations, and are ordinarily considered to be substantially different in kind. Gas separation membranes operate on a molecular scale and fractionate gas mixtures based on size and absorption/desorption characteristics.

An important property of porous membranes is their permeability to flow. In the majority of applications, it is commonly desirable to process effectively the greatest volume of a feed material in the least amount of time. All other things being equal, the higher the flow rate of filtrate or related materials through the membrane, the higher the efficiency and economy of the procedure.

It has long been known that flow rates are proportional to pore diameters, and pore population. Taken together, these define an effective area through which fluids may pass. In practice, the relationship is ordinarily very approximate and highly variable.

Membranes may have a skin or may be skinless, i.e., with an isotropic structure from one face to the other. If a cast liquid film of adequate polymer concentration is quenched in a strong non-solvent, as with polysulfone

solutions (or dispersions) quenched in water, the result is a "skinned" membrane, i.e., one with considerably smaller pores on the "skin" side than on the opposite side. If the quench liquid is a weak non-solvent, e.g.,
5 by adding solvent to the water, a more open skin and ultimately a skinless membrane can be produced.

When a skin is present, as generally in the case with gas separation, reverse osmosis, and ultrafiltration membranes and sometimes with microporous membranes, it is
10 most often a dense film of polymer material with very small pores that extend into a support region of larger pores. If the pores are large enough, they can be observed by electron scanning microscopy, and this is true in the microporous range. However, because of the
15 limitations of SEM techniques pores may not always be directly observable at diameters of less than about 0.050 micrometers, but their presence can be confirmed by the retentivity characteristics of the membrane.

Membranes can have different structures, generally
20 determined by the technique by which it is synthesized. Examples include fibrous, granular, cellular, and spinodal, and they may be symmetrical, or asymmetric, isotropic or anisotropic (i.e., graded pore density).

Fibrous microstructure is most commonly associated
25 with biaxial stretching of films of polymers. This is commonly employed, for example, in the production of porous membranes of polytetrafluoroethylene (TEFLON), in the microporous membranes commercially available as GORETEX, among others. It is inherent in the nature of
30 the process that the result is a skinless, symmetrical membrane.

Granular microstructure can be characteristic of membranes formed by the precipitation of polymer from certain formulations by a nucleation and growth mechanism.
35 Globules or granules of precipitated polymer form and grow, and fuse with other such globules at their points of contact, leaving voids in the interstices which contribute the porosity of the granular mass. Such structures

frequently contain "macrovoids" or "finger voids" in regions adjacent to skin imperfections which allow the quench liquid to penetrate the interior. The voids consequently are also skinned and lead to reduced membrane permeability. This occurs most commonly in ultraporous and reverse osmosis membranes. The techniques for the formation of such membranes are illustrated by Michaels, U.S. 3,615,024. The granular microstructure and characteristic "macrovoids" are illustrated by the photomicrographs shown in Wang, U.S. 3,988,245.

Cellular pore structures which are honeycombed or sponge-like in appearance, are dependent presumably on a precipitation rate that is slower than with granular structures containing macrovoids. They can be skinned or unskinned. The latter structure generally is formed when the precipitation agent is moisture in the air (no liquid quenching during the curing process). A network of thin struts creates the system of contiguous polyhedral shaped cells. Liquid quenched membranes of this type are often associated with a dense or ultraporous skin.

Spinodal microstructure, as mentioned earlier, occurs when the polymer is precipitated by a spinodal decomposition mechanism, characterized by the formation of two separate liquid phases, one polymer rich and the other polymer poor, under conditions wherein each phase is continuous and dispersed in a characteristic pattern at the point at which the polymer precipitation occurs. Depending on the specific characteristics of the technique for attaining the spinodal decomposition mechanism, the resulting membrane may be, on the one hand, skinless, symmetrical, and uniform throughout, or skinned, asymmetric, and non-isotropic.

In the present application, the term spinodal structure is intended to mean the characteristic structure attained when a membrane is precipitated by spinodal decomposition, and to reflect the features illustrated in FIG. 1 and, in different scale, FIG. 8 which illustrate, by SEM photomicroscopy the remaining structure when the

two, intertangled and intermixed continuous phases of spinodal decomposition are achieved. As those of ordinary skill in the art will understand, the spinodal structure represents one of the two continuous phases formed by the precipitated polymer, the other being the void volume within the structure.

The skinless symmetrical variety may be formed by thermal quench techniques or by solvent evaporation techniques. Thermal quenching techniques are illustrated by Castro, U.S. 4,247,498.

Skinned membranes with a highly asymmetric support structure are shown in Wrasidlo, U.S. 4,629,563, and Wrasidlo, U.S. 4,774,039. These membranes are formed by spinodal decomposition induced by solvent extraction from a cast metastable dispersion of two liquid phases, one polymer rich and the other polymer poor, in a liquid quench bath.

All the various techniques involved, and the membranes produced, have achieved a measure of commercial success. The spinodal microstructure, however, has often been preferred in a number of applications. As a general rule, the structure affords good mechanical properties, including tensile strength, elongation at break, and the like, the lowest hydraulic resistance to flow of any of the known microstructures, and offers opportunities to take advantage of the internal structure of the support as a depth filter, as a containment medium for materials, and other like advantages. As is well known to the art, the skinless, symmetric varieties have rather different uses than the skinned, highly asymmetric membranes of Wrasidlo.

In the dispersion casting technique of Wrasidlo, a number of disadvantages have been encountered. These include the following:

When the polymer is precipitated from the dispersion, there are frequent occurrences of small discontinuities. The reason for this is not fully understood, but the result is the formation, within the microstructure of the membrane support, substantial number, and at time vast

numbers of tiny polymer spheres. These discrete spheres are difficult to remove by washing, and substantial numbers may remain in the membrane. This is highly undesirable, in most uses of the membranes, since there are few applications where the introduction of these spheres into a filtrate is acceptable. See the spheres illustrated in FIG. 7, which represent a severe case, after normal washing of the membrane.

The procedure for the formation of the membranes taught by Wrasidlo has over time proved to be excessively variable in the controlling pore diameter, flow rate for a given pore diameter, and in the occurrence of macro flaws in the integrity of the skin, leading to the loss of an unacceptable proportion of the membranes to a failure to satisfy necessary quality control standards. Quality control rejection of such membranes often has been substantial.

Some physical properties, including tensile strength and elongation at break, are often lower than desirable, and lower than required for the integrity of some otherwise desirable uses of these membranes.

These membranes are often employed in critical applications in the electronics industry, food processing, processing of biological materials, as sterilizing filters, and the like. Deficiencies in meeting the quality control requirements of such sensitive fields of use are quite unacceptable.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to improve the technology by which skinned, asymmetric ultraporous and microporous membranes having a support structure with an asymmetric spinodal structure are produced, and to provide such membranes with improved properties and characteristics, and to satisfy the highest standards of quality control and product integrity.

The present invention is intended as, and has as its primary object, an improvement on the process and product

of Wrasidlo, cited above. The disclosure of the Wrasidlo patents is incorporated herein by reference.

In one aspect, the present invention provides an improved method for making the ultraporous and microporous membranes, wherein interaction of the cast dispersion with the atmosphere prior to solvent extraction in a quench bath is limited to less than 0.5 seconds, and preferably less than 0.25 seconds, and where the casting temperature of the dispersion is materially reduced.

In another aspect of the present invention, ultraporous and microporous membranes are produced which are substantially free of polymer spheres entrained in the support, have increased tensile strength and elongation at break, a materially reduced standard deviation in controlling pore diameter, and an increased population of skin pores, resulting in and demonstrated by exceptionally high flow rates in relation to the controlling pore diameter.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a reproduction of an SEM photomicrograph showing the characteristic asymmetric spinodal structure of the support region of membranes of the present invention, in a cross section of a fracture face at an enlargement of 650X.

FIG. 2 is a reproduction of an SEM photomicrograph showing the characteristic skin pores of a membrane of the present invention at an enlargement of 3,000X.

FIG. 3 is a graph showing the relationship of bubble point and flow for membranes of the present invention compared to comparable, historical values for membranes of the prior art, represented by the Wrasidlo patents cited above.

FIG. 4 is a graph showing the relationship of increase in flow rate of the membranes of the invention over the corresponding historical values of production of Wrasidlo membranes of comparable bubble point.

FIG. 5 is a graph of bubble point covariance for membranes of the present invention compared to historical,

corresponding measurements of membranes of the prior art, represented by the Wrasidlo patents cited above.

FIG. 6 is a graph of flow rate covariance for membranes of the present invention compared to historical, corresponding measurements of membranes of the prior art, represented by the Wrasidlo patents cited above.

FIG. 7 is reproduction of an SEM photomicrograph showing a membrane made in accordance with Example II of Wrasidlo, showing the high population of polymer spheres, in a section of the support region at an enlargement of 1,800X. A spinodal structure is apparent.

FIG. 8 is a reproduction of an SEM photomicrograph showing a membrane made in accordance with the present invention, showing the very low population of polymer spheres, in a section of the support region at an enlargement of 1,800X. The spinodal structure of the membrane is shown in detail.

DETAILED DESCRIPTION

The present invention is directed to improved membranes, and to the improved method for making such membranes. In the following discussion, a characterization of the method for making membranes is described and characterized initially.

In the method of the present invention, the process of the Wrasidlo patents, discussed and cited hereinabove, is the starting point of the work, and the relevant disclosure of the Wrasidlo method is accordingly incorporated by reference.

In present method, the major elements which differ from Wrasidlo are found in the limitation of the interaction of the cast dispersion with the atmosphere prior to solvent extraction in a quench bath to less than 0.5 seconds, and preferably less than 0.25 seconds, and the employment of a casting temperature of the dispersion materially less than those commonly employed in the usual techniques, generally on the order of about 6 to 14°C or more. Other process parameters may be subject to adjustment in relation to these parameters to assure the

maintenance of the requisite properties in the membrane produced, but these are generally minor in degree and are reactive to and compensatory for the primary changes in the operating conditions and steps.

5 It has long been known that the cast film of the metastable dispersion in the Wrasidlo technology interacts with the atmosphere, and that the properties of the membrane, and particularly the skin pores of the membrane, are sensitive to variations in temperature and humidity,
10 velocity and direction of air flow, and perhaps others. Controlling these parameters has received a considerable level of attention and, indeed, some have taken steps intended to take advantage of these interactions. See Fuji Photo Film Co. Ltd., G.B. 2, 199,786 A, wherein the
15 exposure and dwell time in the atmosphere and the humidity are increased to attempt to achieve certain benefits. The conventional thinking has been that moisture in the atmosphere initiates the requisite pores at the immediate film/air interface which have diameters proportional to
20 the water vapor concentration and exposure times.

 The view in the art for liquid quenched hydrophobic membrane production has at least in part been influenced by the limitations of the commonly employed equipment used to cast and quench such membranes. In large measure, such
25 equipment has been designed and built on the basis that relatively long exposure times in the atmosphere are generally beneficial. It has been common to employ residence times of atmospheric exposure greater than 1 second, and often longer than 5 seconds. Most equipment
30 cannot attain dwell times between the casting operation and the quench bath of less than 1 second without specific modifications. Since such modifications run counter to the conventional wisdom in the art, there has never been any incentive to do so.

35 It has now been found that residence times of materially less than 1 second, employed with a materially reduced casting temperature, are of quite surprising and unexpected benefit. As discussed in detail below, the

membrane product is quite substantially improved in a number of properties and parameters.

As Wrasidlo has previously pointed out, all the parameters of the casting procedure and the conditions of operation are mutually interdependent. A change of one parameter will require a correlating change in at least one other parameter. If the environmental residence time is reduced, as required in the present invention, to less than 0.5 seconds, and preferably less than 0.25 seconds, for a casting formulation and conditions which had been developed for a longer exposure time, of, say, 1 to 5 seconds, an unsuitable membrane will be obtained if no other parameters are adjusted to balance the effect on the system of the rapid passage into the quench liquid.

It has also been known in the art that for any given dispersion and any given set of casting conditions, there is a relatively narrow casting temperature variance which will be effective. This is generally monitored directly, and correlated with the optical density of the metastable dispersion, in order to produce the desired membrane. If the temperature of the casting dope is too high or too low, unsuitable membrane or even no membrane at all will be produced. In the context of the present invention, the appropriate temperature will be lower than that for the same dispersion when cast at longer environmental dwell times, but it is not possible to define the precise temperature without working trials of the system and confirmation of the results through analytical techniques common to the art. As a general rule, the necessary casting temperature will be on the order of 6 to 14 or more, often on the order of about 10 to 12, °C below the casting temperature appropriate to 1 second environmental dwell time.

The lower casting temperature is an important benefit to the process. It has been learned that lower temperatures make the system less variable and less vulnerable to variation in substantially all parameters. As the temperature gets closer to ambient temperatures, as

one example, distortions of the casting equipment through thermal expansion and like effects are reduced, and it has proved simpler and more reliable to maintain working tolerances. This in turn provides better control over the casting and quenching operations, so that quality of the product is easier to establish and maintain. Utility costs of the operation are reduced and, in new installations, simpler temperature control equipment may prove effective.

10 It is believed, although there is no wish to be bound thereby, that reduced casting temperature plays a direct role in the reduction of polymer spheres entrained in the membrane as an artifact of small proportions of a separately dispersed phase in the casting dispersion. See
15 FIG. 7, which shows such polymer spheres in a prior art membrane. It appears that the spinodal decomposition mechanism operates more uniformly and exclusively at the lower temperatures employed in the present invention, resulting in substantially no incidence of such polymer
20 spheres. It is possible that this result is partly or wholly attributable to some other factor involved in the system, of course, but it remains the case that the high temperature casting of the prior art consistently produced such polymer spheres, and few and often none are observed
25 in the procedure of the present invention.

In practice, the method of the present invention involves the essential steps of mixing a polymer, a solvent, and a non-solvent to produce a metastable liquid-liquid dispersion consisting of a polymer-rich phase and a
30 solvent-rich (polymer-poor) phase within the binodal or spinodal at a casting temperature, casting the dispersion into a thin film at the casting temperature, passing the cast layer within a time of less than 0.5 seconds at the casting temperature into a solvent extraction quench bath
35 of non-solvent quench liquid in which the solvent is freely miscible and in which the polymer is substantially insoluble, and effecting precipitation of the polymer by

spinodal decomposition, and recovering the membrane from the quench bath.

As noted in the Wrasidlo patents, cited above and incorporated herein by reference, a substantial number of polymers, solvents, non-solvents, and quench liquids have been employed, and have been formulated into casting dispersions suitable for casting membranes with a wide spectrum of pore diameters. All of these are contemplated in the present invention. For convenience, the present invention is discussed in the most common of these systems, where the polymer is a polysulfone, the solvent is dimethylformamide, the non-solvent diluent is t-amyl alcohol, and the quench liquid is water.

There are several standard pore diameters which have achieved common commercial acceptance for such polysulfone membranes. These include molecular weight cutoff values of 10,000 and 100,000 Daltons, and pore diameters of 0.1, 0.2 and 0.45 micrometers. The basis for casting the commercially available membranes according to Wrasidlo is shown in Table I:

TABLE I

25	Pore Diameter	10K	100K	0.1 μ	0.2 μ	0.45 μ
	Polysulfone	14-16	12-14	10-12	10-12	10-12
	DMF	80-82	74-76	72-74	72-74	72-74
	t-Amyl alcohol	3-5	11-13	14-16	14-16	14-16
	O. D.	.08-.10	.10-.12	.17-.22	.20-.32	.32-.40
30	Casting Temp.	49-52	49-52	49-52	49-52	49-52
	Time to Quench	1	1	1	1	1

Notes:

35 The polysulfone is Amoco Udell P-3500.
 All proportions are in weight percent.
 O.D. is optical density of the dispersion.
 Casting temperature is given in °C.
 Time to quench is the dwell time in seconds between the doctor blade and the quench bath.

40 The corresponding parameters for the same membranes cast in accordance with the present invention are shown in Table II:

TABLE II

5	Pore Diameter	10K	100K	0.1 μ	0.2 μ	0.45 μ
	Polysulfone	14-16	12-14	10-12	10-12	10-12
	DMF	80-82	74-76	73-75	72-74	72-74
	t-Amyl alcohol	3-5	11-13	14-16	14-16	14-16
	O. D.	.08-.10	.10-.12	.24-.25	.33-.40	.60-.80
10	Casting Temp.	35-43	35-43	35-40	35-39	35-39
	Time to Quench	0.1	0.1	0.1	0.1	0.1

Notes:

- 15 The polysulfone is Amoco Udell P-3500.
 All proportions are in weight percent.
 O.D. is optical density of the dispersion.
 Casting temperature is given in °C.
 Time to quench is the dwell time in seconds between the doctor
 blade and the quench bath.

20

As those of ordinary skill in the art will readily recognize, the residence time between the casting operation and the quench bath is reduced by one order of magnitude. A reduction in casting temperature on the
 25 order of about 10°C is also imposed. In a more general sense, the dwell time should be kept below 0.5 seconds, and preferably below 0.25 seconds, and is desirably the minimum that can be achieved with the constraints of the casting equipment employed.

30 The casting dispersion should, as noted in the Tables, have an optical density of from about 0.5 to 1, depending on the pore diameter sought; generally, higher optical densities produce higher pore diameters.

35 The casting dispersion is ordinarily cast onto a moving support by means of a doctor blade with a knife gap of typically about 250 to 450 micrometers, often about 300 micrometers; after the quench, the membrane produced is typically about 85 to 105 micrometers in thickness for
 40 microporous membranes. The values may be increased or decreased as desired, as is well known in the art. While as described, the procedure produces flat sheet membrane, the present invention is equally applicable to casting

hollow fiber membrane, and will indeed facilitate the dispersion casting operation by reducing or even eliminating the atmospheric exposure time previously thought to be necessary to such procedures.

5 In application of the present invention to the casting of hollow fiber, the casting dispersion is spin cast through a hollow die rather than being cast onto a support in a flat film form. The lumen of the hollow fiber is sometimes formed by air or inert gas and the
10 outside quenched in non-solvent liquid, but usually the quench liquid flows through the center and skins the Lumen. If the lumen is formed by a gas, it should be introduced as close to the quench bath as possible. As those familiar with hollow fiber casting are aware, the
15 die may be immersed in the quench bath in some cases, reducing the atmospheric dwell time of the outer surface of the cast membrane to zero. It is possible, of course, to provide a hollow fiber with both inner and outer skins by employing the quench liquid in both the lumen and the
20 quench bath.

The cast dispersion is passed into a quench bath, most commonly of water, frequently at or near the casting temperature. In the bath, the quench operation precipitates the polymer to produce a skin having the
25 requisite pore sizes, and a support region having the characteristic spinodal structure with a high degree of asymmetry, increasing from the region immediately adjacent to the skin to the opposite face. The resulting membrane is ordinarily washed to free it of entrained solvent, and
30 may be dried to expel additional increments of solvent, diluent, and quench liquid, and thus recover the membrane.

The casting operation is amenable to a wide variety of known variations, familiar to those of ordinary skill in the art, as discussed by Wrasidlo and others in the
35 prior art. So long as the criteria defined for the present invention are met, none of these are excluded.

The resulting membrane produced by the process of the present invention shares a number of characteristics in

common with those taught by Wrasidlo and used in commerce in the practice of his technology. There are substantial differences which are attained, however.

5 It is a very great advantage of the improvements provided by the present invention that the membrane is produced substantially free of the artifacts of discontinuous dispersion in the casting medium. To date, only negligible numbers of polymer spheres have been observed in membranes cast by the method of the present invention. Compare the membrane of the present invention shown in FIG 8 with FIG. 7, showing the prior art problem, which is now largely resolved. The requirement for the removal of such materials as a part of the membrane wash operations is now eliminated or greatly reduced, reducing 10 the time of the wash, the amount of water or other wash constituents is reduced substantially, and production of finished product are simplified.

It is another significant achievement of the present invention that the pore diameter of the skin pores is far more consistent, as shown by bubble point testing. Testing of membranes of the present invention shows that the bubble points desired are achieved far more readily and consistently at all points in the casting operation, from start-up to conclusion, with markedly reduced standard deviation in pore diameter for all pore sizes. Pore diameter is the primary quality control parameter in such membranes, and bubble point is the convenient parameter for defining microporous membrane integrity, the ultimate criteria being bacterial or microsphere challenge tests. 20 25 30

Indeed, for most pore diameters, it is now possible to maintain production at bubble point measurements having a standard deviation of less than 3, compared to a historical value of about 5 or more for such membranes, although in smaller pore sizes it may be necessary to accept a slightly higher standard deviation of less than 5, compared to a historical value of 9 or more for comparable membranes. Covariance in bubble point is less 35

than 8, and ordinarily and preferably less than 5, compared to historic values of 9 or higher, and most often above 11 or even higher, as illustrated in FIG. 5. The skin pores are illustrated in FIG. 2, revealing both a high population of pores, a large proportion of which are at or near the effective controlling pore diameter.

Another feature of the membranes of the present invention is the material increase in flow rates for a given controlling pore size. While the relationships and physical features of the membrane of the present invention which determine flow rates have not been fully explored as yet, the data show a substantial increase in flow rate as a function of pore diameter (or pore radius, as discussed in Wrasidlo). The data suggest an increase in the total number of pores produced in the membrane skin, and possibly a narrower distribution of pore diameter, with few pores having a diameter materially less than the controlling pore diameter as determined by bubble point measurements. See FIG. 2.

What the data do show with certainty is represented in the data plotted in FIG. 3, which demonstrates flow rate plotted against pore diameter, for the membranes of the examples provided in the present application, including the comparative examples. It is apparent that at a given pore diameter, the flow rate is materially increased in the present invention, when compared to the historical values achieved by the Wrasidlo teachings.

In addition, the flow rates are less susceptible to variation during manufacture of the membrane, as reflected by a standard deviation in flow rate of normally about 120 or less, more often about 100 or less, and less than 75 except for the largest pore diameters. This improved consistency at the higher flow rates is indicative of a material change in the utility of these membranes for the user, and enables the present invention to assure higher levels of quality assurance to users, particularly those with critical applications for such membranes. As shown in FIG. 6, covariance of flow rates of the membranes made

by the new procedures of the present invention are less than 6, and for most pore diameters, less than 5. FIG. 6 also demonstrates that flow rate covariance of membranes made by the Wrasidlo procedure has historically been greater than 12.5. Standard deviations are materially reduced as well,

The consistency achieved in the present invention is a *per se* benefit in the production and use of the membranes of the present invention, and represents a very substantial gain in productivity and the reduction of scrap or out-of specification materials. The occurrence of scrap has been reduced to a level consistently less than 5% of production, and long production runs with no losses to scrap are now frequently attained. The improved consistency is also of compelling import to the integrity of the membrane offered to users.

As shown in FIG. 4, the improved consistency in pore diameter and in flow rate are accompanied by a material increase in the flow rate for each pore diameter, ranging from an increase in flow rate of from 110 ml/min. at a bubble point of about 65, up to about 500 ml/min. at a bubble point of about 30, representing a gain in flow rate of 10 to 20 percent at a given pore diameter.

A photomicrograph showing the characteristic spinodal structure of the membranes of the present invention is shown in FIG. 1. As those of ordinary skill in the art will recognize, the structure is that produced by spinodal decomposition of the metastable dispersion in the membrane casting operation, and the figure illustrates the significant asymmetry which makes such membranes highly effective as depth filters, affording the gradual change in the apertures through the support region such that the changing effective pore diameter is progressive.

The skin of the membrane is quite thin, and difficult to delineate precisely by photomicroscopy in cross section. Where skin pores are directly observable, as shown in FIG. 2, the number of pores and their general regularity is directly observable.

A number of membranes have been made and tested in accordance with the present invention, and compared with the commercially available embodiments of the Wrasidlo technology. These efforts and comparisons are set out in the following examples.

SPECIFIC EXAMPLES

In the following examples, the formulations employed are those set forth in Table I and Table II, above. The conditions of casting are also those set forth in the tables. Both the examples of the present invention and those based on the Wrasidlo teachings were performed on the same equipment, and under the same conditions; the only differences are those set forth in the above Tables. As inspection will show, no adjustments of the formulations to achieve specifically targeted pore diameters were made in most cases, with the results that some of the bubble point values are higher than desired. Further adjustments to achieve the desired bubble point, reflecting a specifically required pore diameter are known to the art, and are specifically taught by Wrasidlo.

A plurality of rolls of membrane were cast. Each roll was sampled at a plurality of predetermined locations, across the web and throughout the length of the cast membrane. The values for each sample were averaged, and the standard deviation determined, for both bubble point and flow rate. The results obtained are shown in the following Table III:

30

TABLE III

	<u>Example</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
35	30-1	2393	113	38	0.8	548	21	26	3
	30-2	2495	100	38	0.6	535	14	30	2
	30-3	2340	73	36	1.6	544	5	30	3
	30-4	2311	45	37	1.1	518	16	27	2
	30-5	2097	73	38	0.7	578	14	30	1
40	30-6	2337	184	38	2.6	607	9	29	2
	30-7	2232	98	38	1.4	607	23	26	3
	30-8	2402	74	36	2.1	600	23	24	4
	30-9	2470	77	36	1.3	558	10	24	2

TABLE III, cont.

	<u>Example</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
5	30-10	2586	75	35	2.3	569	8	24	2
	30-AVE	2366	91.2	37	1.45	566	14.3	27	2.4
10	<u>Example</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
	45-1	1663	110	45	3.1	552	20	29	3
	45-2	1776	83	44	2.9	536	8	29	3
	45-3	1495	50	49	3.5	521	13	31	2
15	45-4	1525	38	47	2.1	523	8	29	5
	45-5	1635	53	45	0.8	538	9	32	3
	45-6	1671	42	44	1.6	525	11	29	2
	45-7	1705	56	44	2.2	530	22	29	3
	45-8	1720	75	44	1.3	529	7	36	1
20	45-9	1742	73	44	3.3	520	19	34	5
	45-10	1778	59	42	2.2	504	11	28	2
	45-11	1673	114	46	1.4	556	14	25	3
	45-12	1844	79	43	3.2	548	10	34	4
	45-13	1737	118	47	1.5	554	24	30	5
25	45-14	1805	52	46	2.0	561	8	33	2
	45-15	1697	76	48	1.4	554	15	32	3
	45-16	1761	87	48	3.0	528	9	29	2
	45-17	1608	76	48	2.5	584	12	34	2
	45-18	1779	44	46	3.6	569	15	32	2
30	45-19	1556	53	48	1.7	545	16	32	3
	45-20	1698	32	45	1.5	547	16	32	3
	45-21	1626	95	48	1.4	513	18	32	3
	45-22	1802	43	44	1.7	488	18	30	3
	45-23	1657	123	42	3.2	568	6	31	2
35	45-24	1747	54	45	3.2	561	17	31	4
	45-25	1534	108	48	1.6	578	19	29	3
	45-26	1630	84	46	2.5	561	17	29	4
	45-27	1634	70	47	2.2	572	13	27	3
	45-28	1787	57	44	1.8	558	17	29	3
40	45-AVE	1689	71.6	45.6	2.2	544	14	31	3.0
45	<u>Example</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
	55-1	1234	45	57	3.0	574	23	36	5
	55-2	1296	64	64	1.8	573	14	30	3
	55-3	1192	47	59	3.0	612	16	34	4
	55-4	1228	66	58	2.0	595	9	34	2
50	55-5	1359	101	54	2.9	619	11	34	2
	55-6	1418	26	52	2.4	598	20	36	4
	55-7	1271	97	56	4.0	600	13	39	3
	55-8	1319	55	57	2.7	588	16	38	2
	55-9	1284	76	58	4.2	613	25	35	6
55	55-10	1364	57	57	2.5	609	25	35	4
	55-11	1561	97	48	2.3	523	20	29	5
	55-12	1598	66	49	2.3	555	17	32	4
	55-13	1258	103	56	2.8	553	11	39	4

TABLE III, cont.

	<u>Example</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
5	55-14	1439	36	53	1.4	579	15	35	4
	55-15	1253	87	56	3.0	533	23	28	4
	55-16	1363	67	54	1.0	573	13	35	3
	55-17	1387	39	56	2.3	615	12	38	2
	55-18	1430	60	55	3.2	586	20	37	4
10	55-19	1300	47	56	1.7	520	23	34	6
	55-20	1410	49	56	1.5	548	25	39	3
	55-21	1290	61	55	3.5	571	11	33	4
	55-22	1418	60	54	0.9	590	26	35	4
15	55-AVE	1349	63.9	55.5	2.47	578.5	17.6	34.8	3.7
	<u>Example</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
20	65-1	1146	50	60	2.5	676	22	39	4
	65-2	1403	22	60	2.4	665	24	40	4
	65-3	1108	57	59	3.7	648	17	44	4
	65-4	1115	36	62	1.5	637	26	36	5
	65-5	1060	65	60	3.6	613	29	34	5
25	65-6	1155	40	60	2.5	610	21	33	3
	65-7	1013	46	64	4.4	666	19	35	2
	65-8	1037	30	68	2.8	697	20	36	3
	65-9	859	93	72	12.0	664	31	39	2
	65-10	854	77	78	8.4	648	24	36	3
30	65-11	986	76	64	7.6	614	35	35	7
	65-12	931	82	73	7.5	616	37	36	5
	65-13	949	61	65	6.4	713	27	33	4
	65-14	1026	75	62	6.9	694	25	33	4
	65-15	1046	79	59	2.1	695	24	35	5
35	65-16	1095	47	57	2.5	684	23	34	4
	65-17	1217	94	55	5.3	642	12	38	4
	65-18	1346	50	52	4.8	638	23	38	3
	65-19	1019	37	61	2.1	657	12	37	2
	65-20	1146	59	58	1.7	658	18	38	3
40	65-21	1017	50	63	3.4	674	14	36	4
	65-22	1101	40	60	3.4	688	18	38	4
	65-23	932	83	72	9.4	668	9	34	2
	65-24	1041	46	63	5.8	630	17	32	3
45	65-AVE	1058	58	62.8	4.7	658	22.0	36.2	3.7

In the foregoing data in Table III, each Example represents a roll of membrane, made as described above, bubble point (BP) is reported as the arithmetic mean of all quality control samples taken for each roll. The bubble point represents the pressure, in psi, of breakthrough of air applied to a 90 mm disc sample wetted with distilled water, common to the membrane art. Flow is reported as the arithmetic mean of all samples for each

roll and represents the flow of distilled water, in ml per minute, passing through a 90 mm disc at an applied pressure of 10 psi. BRK represents tensile strength at break in grams, while ELG is elongation at break, in percent.

**TABLE IV
COMPARATIVE EXAMPLES**

	<u>TYPE</u>	<u>Flow</u>	<u>σ</u>	<u>BP</u>	<u>σ</u>	<u>BRK</u>	<u>σ</u>	<u>ELG</u>	<u>σ</u>
10	X65-AVE	972	129.8	63.1	9.3	588	24.6	29.0	3.2
15	X55-AVE	1278	181.9	51.0	6.9	512	19.8	24.7	2.2
	X45-AVE	2059	403.0	33.8	4.4	491	35.7	23.7	3.1
	X30-AVE	2518	322.6	29.2	2.6	467	26.0	21.8	2.4
20	X25-AVE	3558	481.0	22.8	2.6	469	22.8	23.3	2.3

In Table IV, the values reported for each comparative example, the values reported are the arithmetic mean of all values for actual commercial production of a substantial number of rolls of membrane, produced as indicated in Table I, under the same conditions as those employed in the present invention, except as noted above.

The principles, preferred embodiments, and modes of operation of the present invention have been described in the forgoing specification and examples. The invention is not intended to be constrained thereby, or construed as limited to the particular forms disclosed, since these are intended to be illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit and scope of the present invention as defined in the following claims.

CLAIMS

What is claimed is:

1. A method of making a highly asymmetric integrally skinned polymer membrane, said method
5 comprising:

A. mixing a polymer, a solvent and a non-solvent to produce a metastable liquid-liquid dispersion within the binodal or spinodal at a casting temperature, and having an optical density of
10 from about 0.5 to about 1,

B. casting said dispersion into a thin layer at said casting temperature,

C. passing said cast layer within a time of less than 0.5 seconds at said casting temperature into a solvent extraction quench bath of non-solvent
15 quench liquid in which said solvent is freely miscible and in which said polymer is substantially insoluble, and effecting precipitation of a major proportion of said polymer by spinodal decomposition,
20 and

D. recovering from said quench bath a membrane.

2. The method of claim 1 wherein said time is less than about 0.25 seconds.

3. The method of claim 1 wherein said time is not
25 more than about 0.1 seconds.

4. An asymmetric integral skinned polymer membrane comprising:

A. a porous skin having skin pores with a
30 controlling diameter within the range of from about 500 MWCO to about 0.5 micrometers, and a standard deviation of pore diameter, as determined by the bubble point method, of less than 3,

B. a support region having a highly asymmetric
35 spinodal structure,

C. said membrane having a standard deviation of flow rate of less than about 100 and a flow rate covariance of less than about 6.

5. The membrane of claim 4 wherein said polymer is a polysulfone.

6. The membrane of claim 5 wherein said membrane has a standard deviation of flow rate of less than 75 and
5 a flow rate covariance of less than about 5.

7. A membrane product which is the product of the process of claim 1.

FIG. 1



FIG. 2

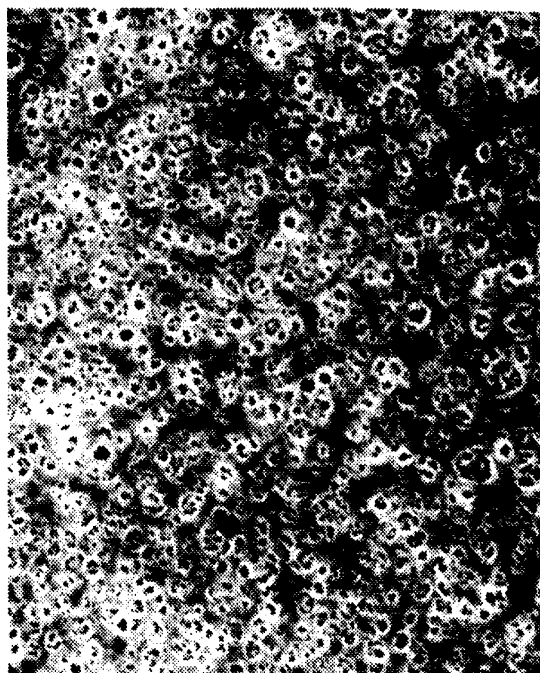


FIG. 7

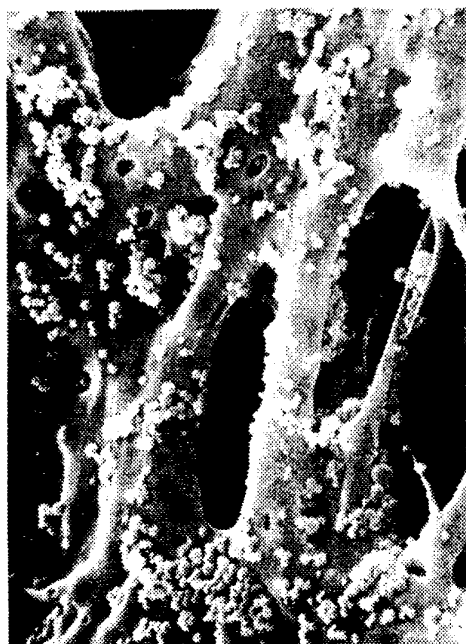


FIG. 8



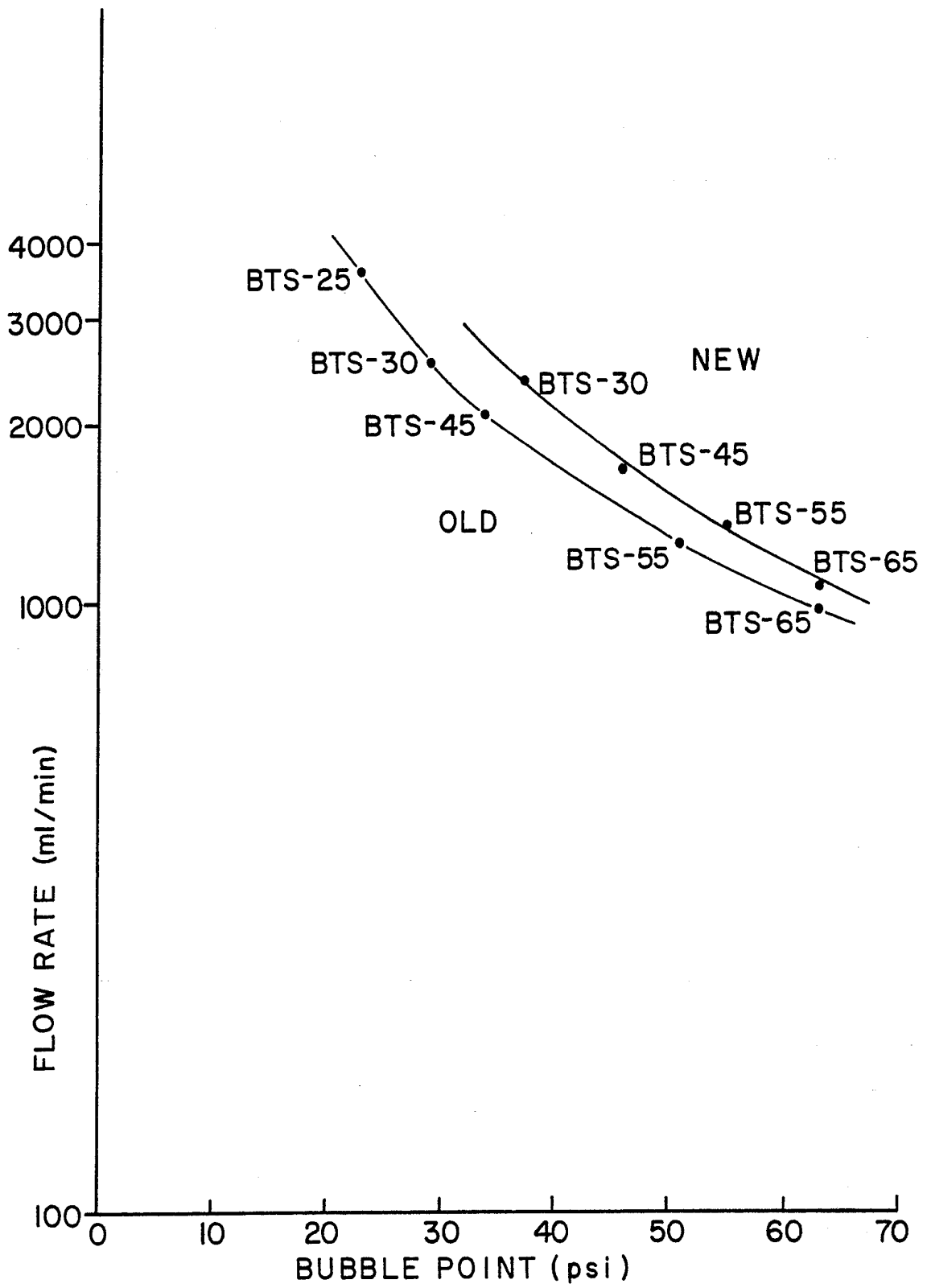


FIG.3

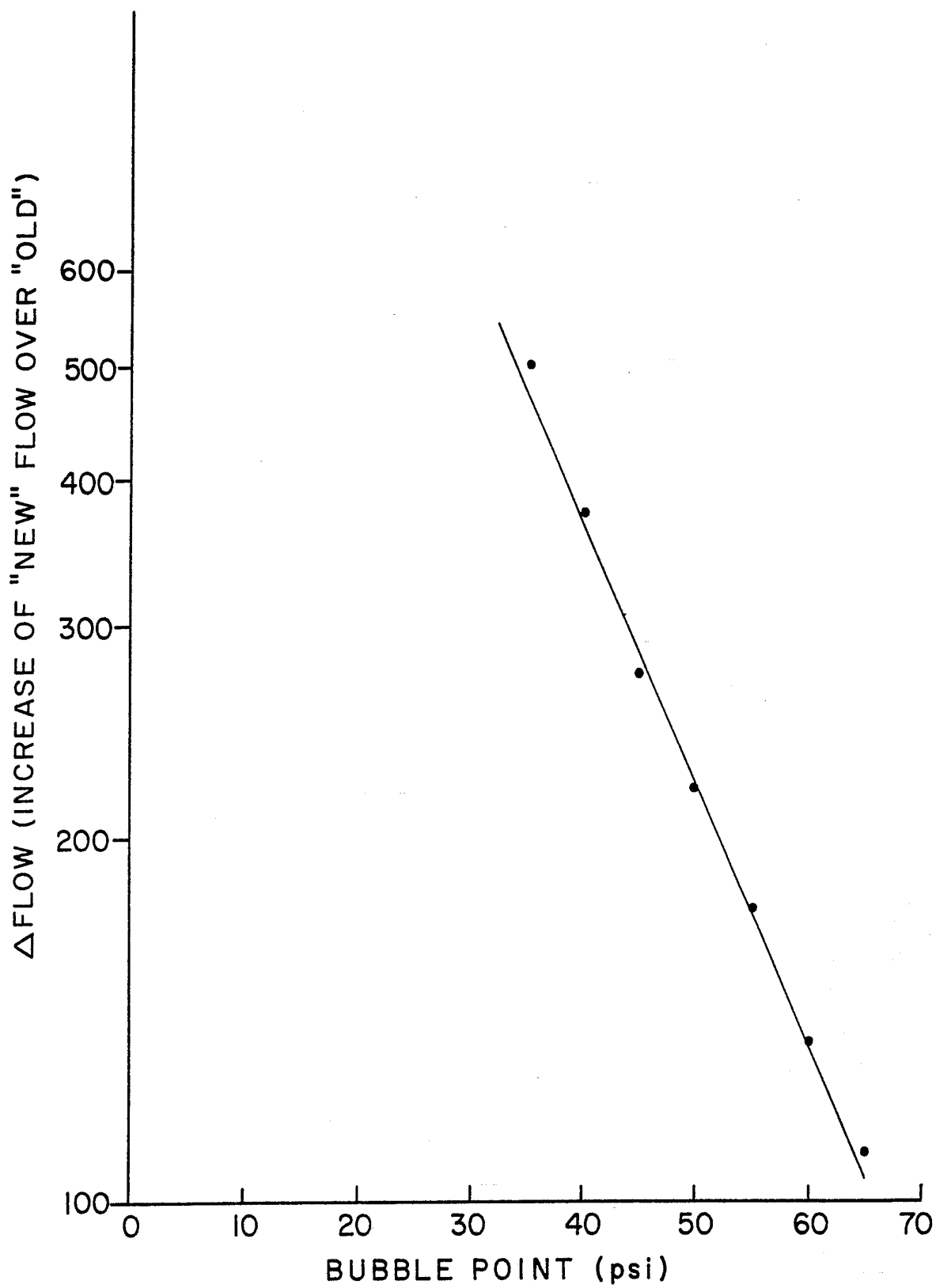


FIG. 4

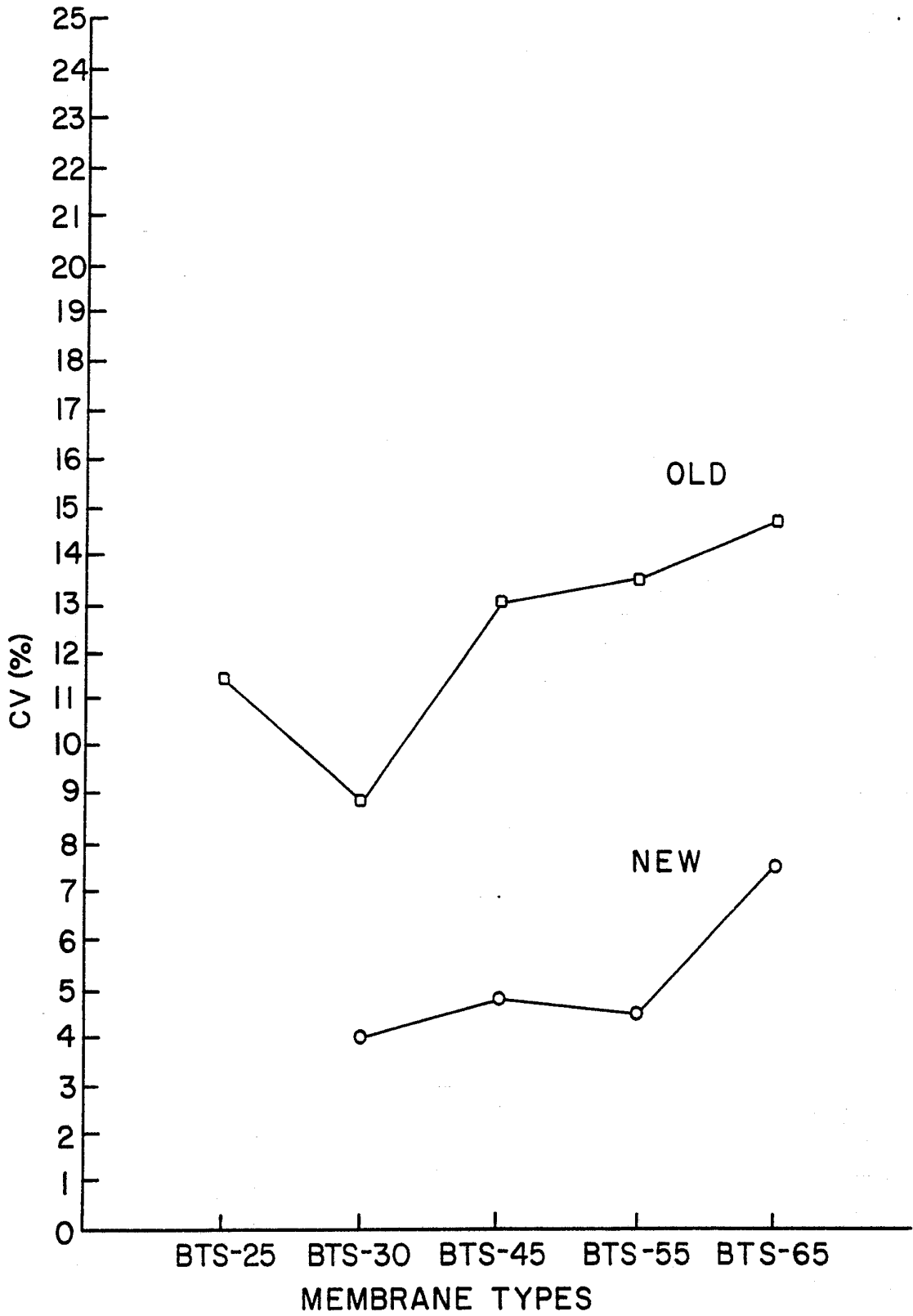


FIG. 5

5/5

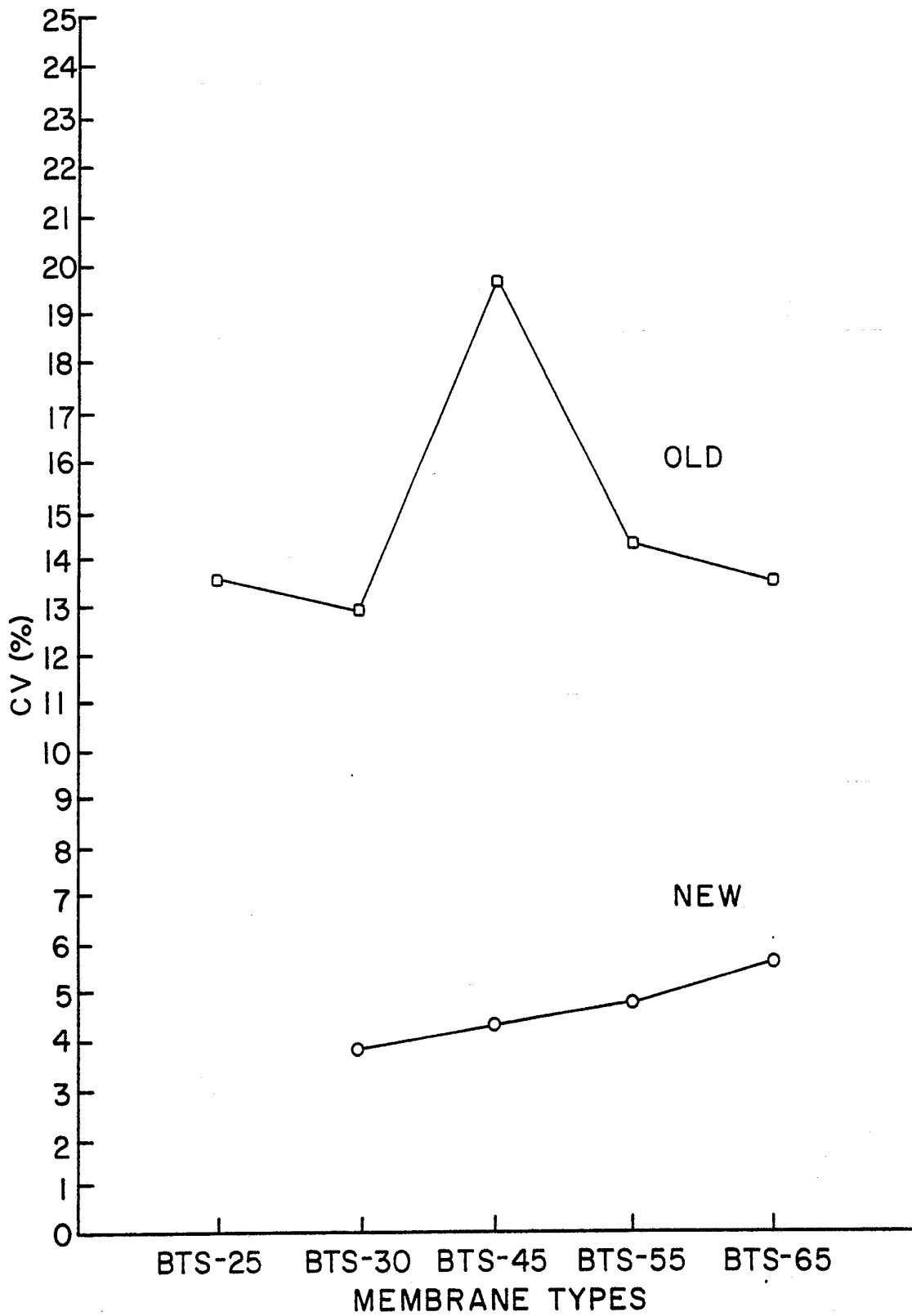


FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01975

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(5): B01D 39/00		
U.S. CL.: 210/500.27		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	210/490, 500.41, 500.38	
	264/41, 45.1, 28, 45.9	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4,774,039 (WRASIDLO) 27 September 1988, See the entire document.	1-3, & 7
A	US, A, 4,629,563 (WRASIDLO) 16 December 1986, See the entire document.	1-3, & 7
A	US, A, 3,883,626 (KAMIDE) 13 May 1975, See abstract column 6, lines 1-68, and column 7, lines 1-52.	1-3, & 7
A	US, A, 4,247,498 (CASTRO) 27 January 1981, See abstract, column 54, lines 56-68, and columns 55-56.	4-6
A	US, A, 3,158,532 (PALL) 24 November 1964, See column 2, lines 27-60.	1-3, & 7
<p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
22 JUNE 1992		14 JUL 1992
International Searching Authority		Signature of Authorized Officer
ISA/US		<i>ANA FORTUNA</i> ANA FORTUNA INTERNATIONAL DIVISION

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

- | | | |
|---|--|-----|
| A | US, A, 4,814,082 (WRASIDLO)
21 March 1989, See column
22, lines 10-68, and columns
23-26. | 4-6 |
| A | US, A, 4,814,082 (WALCH)
21 October 1980, See abstract. | 4-6 |
| A | US, A, 4,220,543 (YAMASHITA)
02 September 1980, See abstract. | 4-6 |

V OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

- 1 Claim numbers _____ because they relate to subject matter ¹⁴ not required to be searched by this Authority, namely:
- 2 Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹⁵, specifically:
- 3 Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

- 1 As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
- 2 As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
- 3 No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
- 4 As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
- No protest accompanied the payment of additional search fees.

III DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4,177,150 (INOUE) 04 December 1979, See abstract, columns 1-10.	4-6
A	US, A, 3,988,245 (WANG) 26 October 1976, See the entire document.	4-6
A	US, A, 3,709,774 (KIMURA) 09 January 1973, See column 2, lines 25-64.	4-6