In addition, the tube edges were glazed with a silica/zirconia glass to prevent direct flow of gas through the tube ends. The tube interior is glossy and free of gross indentations, pits and streaks. Quantitative characterization of such defects in tube production has not been achieved yet.

Finally, the cost estimate provided by the supplier indicated that the tube cost would be within the Air Products set target.

3.3 Define Membrane Preparation Process

A membrane preparation process that coats the SSF membrane on the interior surface of the porous alumina tube was developed, the key steps for which are shown in **Table 5.** In the membrane preparation process, the tube is first cleaned with high pressure nitrogen to remove loose particles from the tube interior and is then conditioned at 100 C to remove most of the water in the larger pores. The membrane precursor, PVDC, is coated on the tube interior by a fill-and-drain sol-gel process in which the tube is filled with the emulsion, held for a fixed length of time and drained through a fixed size orifice (**Figure 7**). The PVDC sol is converted to a gel layer at the liquid-solid interface by capillary suction of the water into the membrane porosity. The coating thickness is primarily controlled by (i) the solids content in the emulsion, (ii) the tube porosity characteristics and (iii) the liquid hold time. After the emulsion is drained from the tube, the coating is dried by holding the tube vertically. Slow convective drying occurs in this step. The PVDC coating is then tested for its average thickness by measurement of the mass of polymer deposited. The quality of the tube coating is evaluated by measuring the permeation of helium or nitrogen through the coating, the equipment for which is shown in **Figure 8**. A good coating ensures a very low permeation (< 20 scc/s.cm2.cm.Hg) of helium through the membrane. Tubes with acceptable PVDC coating are pyrolyzed at 600 -1000 C in an inert atmosphere. During the cooling cycle, the membrane is passivated by reaction with oxygen at 350 C. This prevents membrane degradation with time which would otherwise occur by slow reaction with ambient moisture and air. A glossy, uniform thin layer membrane that adheres extremely well to the alumina support is obtained by this preparation technique. The details of the key steps identified in **Table 5** are discussed below.

3.3.1 Tube Conditioning

Three different techniques for removing loose particles on the tube interior surface were evaluated: (i) blowing with high velocity air/nitrogen, (ii) ultra-sonic cleaning with distilled water and (iii) ultra-sonic cleaning with isopropanol. No significant differences in PVDC coating quality between the different cleaning methods (other than no cleaning) were observed, as shown in **Table 6**. Blowing with high velocity nitrogen was adopted as the standard procedure because of the short operation time.

Tube pre-drying at 100 C was adopted as a standard to ensure that all the tubes were dry to the same extent. Varying moisture levels in the porosity would vary the capillary suction in the tube and hence produce varying coating thicknesses.

TABLE 5

MEMBRANE PREPARATION PROCESS STEPS

Coating of Alumina Tubes

Tube Conditioning :

1. Tube cleaning
2. Tube pre-conditioning

Emulsion Preparation :

1. Diluted Emulsion
2. Filtration at point of use

PVDC Coating :

1. Tube filling with emulsion and drainage
2. Drying
3. Test quality of PVDC coating

Preparation of Carbon Membrane

Pyrolysis of PVDC :

1. Heating and cooling cycle
2. Test SSF Membrane

FIGURE 7

COATING OF TUBE INTERIOR

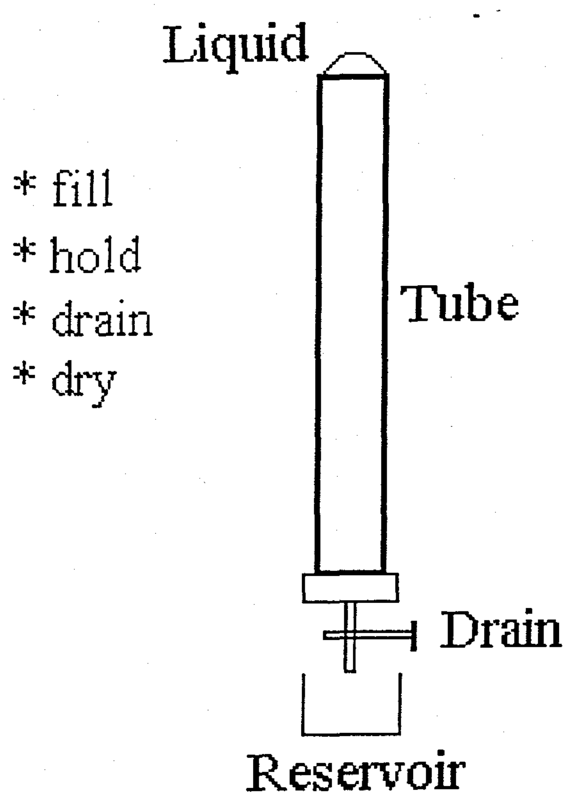


FIGURE 8

MODULE FOR TEST OF PURE AND MIXED GAS PERMEATION

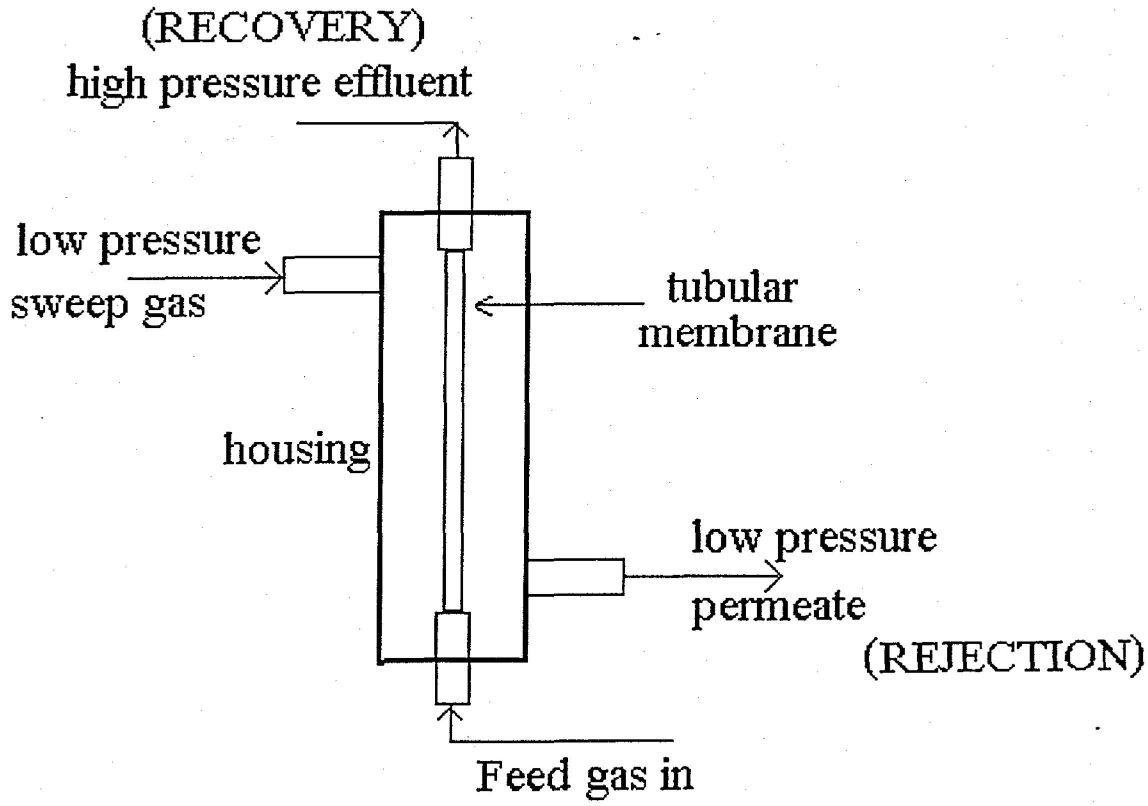


TABLE 6

EFFECT OF TUBE PRE-CLEANING ON PVDC COATING QUALITY

Coatings from 3.4% emulsion with different lots of alumina tubes

Pre-cleaning	PVDC Coating Thickness micron	Helium Permeance $scc/s.cm^2.cm\ Hg \times 10^{-5}$
As-is	6.5	350-30*
High Velocity N_2	6.1	19
Water Wash	6.6	22
High Velocity N_2	12.4	9.8
Iso-propanol Wash	11.7	10.2

Coating thicknesses and He permeances averages of several samples

Coating thickness calculated from weight of coating on tube and a specific gravity of 2.6 g/cc

*Permeances were highly variable without precleaning

3.3.2 Emulsion Preparation

The PVDC used for coating is a water-based emulsion (Daran 8600C, Hampshire Chemical Company, MA). The as-received emulsion contains 51% solids which is diluted to <10% solids with distilled and de-ionized water. The diluted emulsion is prepared by low intensity mixing of the as-received emulsion and water at room temperature. The emulsion is stored for < 1day and is used once-through (i.e., no reuse after drainage from the tube).

The diluted emulsion is filtered at the point of use through a combination of 5 μ and 2 μ filters in series and used directly for coating. This ensures that the largest contaminant particle is smaller than the membrane coating thickness. The filters are replaced once they are clogged.

3.3.3 PVDC Coating

The PVDC coating (precursor to the carbonized membrane) is done by filling the tube with the filtered diluted emulsion, holding for a fixed length of time and then gravity draining. The significant variables affecting the coating thickness are : (i) solids content in the emulsion, (ii) porosity in the tube and (iii) hold time prior to drainage. The specific effects of these variables were evaluated to obtain a defect-free membrane in a single coating as opposed to previous demonstration of the sheet membrane by multiple coats of the carbon film.

Table 7 shows the effect of emulsion solids content on the coating thickness. The data show that the coating thickness increases almost linearly with increased solids content in the emulsion in the range of emulsion solids content investigated. In addition, it has been observed that the coating thickness is strongly affected by the total porosity in the tube. **Table 8** shows the effect of porosity (at the same pore size) on the coating thickness. The coating thickness changes highly non-linearly with the porosity in the tube, with larger PVDC coating thickness on a more porous tube. The coating thickness is controlled by the capillary suction of the water into the tube and the formation of a PVDC gel layer on the tube interior. The fact that capillary effects are significant is shown in **Table 9,** which shows the effect of pre-filling the tube porosity with water prior to coating. The coating thickness is reduced by an order of magnitude by the elimination of water removal capability from the emulsion sol by capillary suction in the alumina tube porosity.

The wall thickness of the tube also changes the total capillary volume and hence impacts the coating thickness. **Table 10** shows the effect of tube wall thickness on coating thickness for tubes with the same pore size and porosity. The data expectedly show that the thicker wall tube causes the coating thickness to be greater (note : a thicker wall has a greater total pore volume available and hence more of the dilute emulsion can achieve a solids content which causes the polymer to gel). Hence, once the wall

TABLE 7

EFFECT OF SOLIDS CONTENT IN EMULSION ON THE PVDC COATING

Data with Lot 2 and 3 tubes

Solids Content %	Weight PVDC coating, g	PVDC thickness micron	Helium Permeance scc/s.cm^2.cm Hg x 10^{-5}
2.5	0.0346	3.0	103
3.0	0.0770	6.5	49
3.4	0.0820	7.0	35
6.8	0.1655	14.1	15
13.8	0.3946	33.7	6

TABLE 8

EFFECT OF TUBE POROSITY ON COATING THICKNESS

BASIS :

Tubes with varying porosity but constant pore size
Coating form 3.4 % emulsion

Tube Porosity %	Pore size micron	PVDC Coating Thickness micron
22	0.256	5.1
24	0.251	8.0
27.5	0.274	11.1

TABLE 9

CAPILLARY EFFECTS ON PVDC COATING THICKNESS

All coatings on lot 2 and 3 Tubes

Solids in Emulsion %	Weight PVDC Coating, g Dry Tube	Tube wall filled with Water
3.4	0.0820	0.008
6.8	0.1655	0.015
13.8	0.3946	0.041

TABLE 10

EFFECT OF TUBE WALL THICKNESS ON COATING THICKNESS

Lot 4 and 5 tubes
All coatings from 3.4% emulsion

Wall thickness	Tube Porosity, %	Pore size, μ	Coating thickness, μ
2.0 mm	26.2	0.275	12.2
1.5 mm	27.5	0.274	8.8

thickness is specified based on mechanical strength requirements, the wall thickness needs to be controlled to obtain a consistent product.

Table 11 shows the effect of hold time of the emulsion in the tube on the PVDC coating thickness. The data show that the hold time is not a strong variable with this pore size and porosity tube, though there is a small increase in the coating thickness after the emulsion is held in the tube for 15 minutes. This observation is supported by the strong effect of initial capillary suction in rapidly forming a polymer gel layer which controls the coating thickness. Two minutes hold time was selected for coating operations. It may be possible to reduce this in manufacturing operation where the coating operation would be a mechanical process rather than the current manual process.

A typical PVDC coating on the alumina tube is shown in the SEM micrograph in **Figure 9**. The coating is about 18 micron thick and uniform under the specific preparation conditions used.

In summary, the data show that the PVDC coating thickness and quality on the porous support can be controlled by several process as well as tube related variables. The optimal coating for the SSF membrane is obtained by a combination of these variables.

3.3.4 Pyrolysis of PVDC

The SSF membrane is prepared by the pyrolysis of PVDC at an elevated temperature in an inert environment. **Figure 10** shows a thermogravimetric analysis (TGA) trace of the decomposition of PVDC coated on an alumina tube in a nitrogen environment. The pyrolysis occurs in three different stages as shown in **Figure 10**. The bulk of the dehydrohalogenation occurs from 120 C to about 250 C. A second weight loss occurs around 290 C, and pyrolysis is complete at 550 C. The mass loss accompanying pyrolysis is 75% (note : mass loss shown in **Figure 10** includes the mass of the alumina support and hence does not show the mass loss from the film alone). It has been determined that the secondary mass loss peaks are critical in the final pore size control since membranes pyrolyzed at intermediate temperatures do not have the desired gas separation properties. The mass loss during pyrolysis shrinks the thickness of the film. For example, an 18 μ PVDC results in a carbon membrane with a thickness of ~4 μ **(Figure 11)**. No significant difference in membrane separation properties was observed in the pyrolysis temperature range of 600 C-1000 C for membranes prepared on tubes. 600 C was chosen as the temperature for pyrolysis.

An initial objective was to determine the minimum PVDC coating thickness required to produce a uniform defect-free carbonized membrane film on the alumina support in a single coating. PVDC coatings were prepared from emulsions with varying solids content and pyrolyzed at 600 C. The following observations and conclusions were made from these experiments:

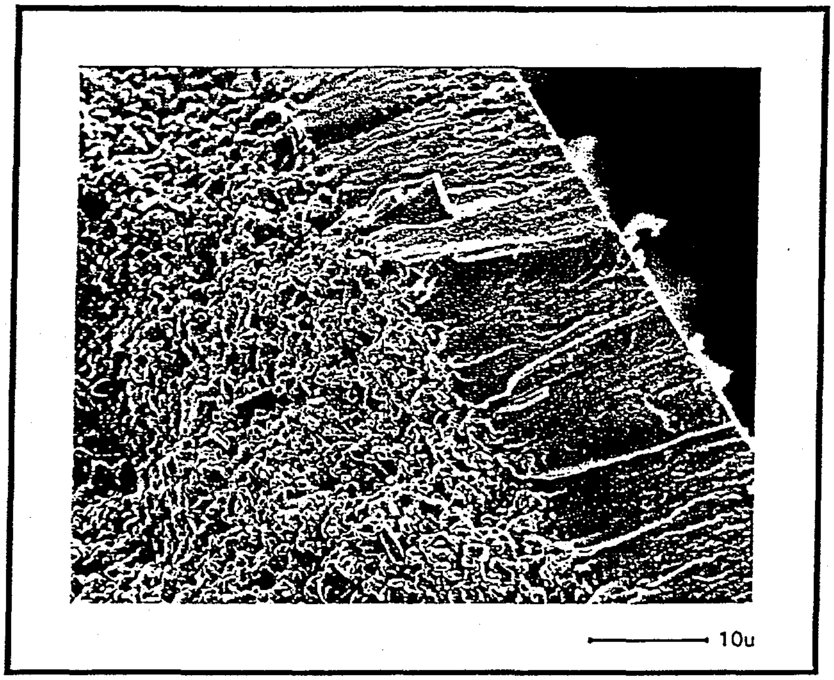
(i) Smooth, highly glossy carbon coatings are obtained when the PVDC coating thickness is < ~15 μ **(Figure 12)**.

TABLE 11

EFFECT OF HOLD TIME ON COATING THICKNESS

All coatings done on lot 2 and 3 tubes with 3.4% emulsion

Hold Time	Weight PVDC, g	Coating Thickness, µ
1 min	0.0869	7.4
2 min	0.0820	7.0
15 min	0.1018	8.7



Title PVDC Alumina 14006-19-3 MA1932 **Date** 05-12-94 **Time** 14:22
Comment *cross-section area 2*
Mag X2,000 **kV** 5 **WD** 10mm **Spot** 6 **Scan** P3

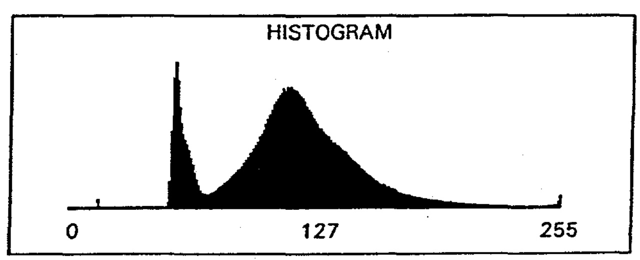


Figure 9. SEM Showing Uniform PVDC Coating on Alumina Tube

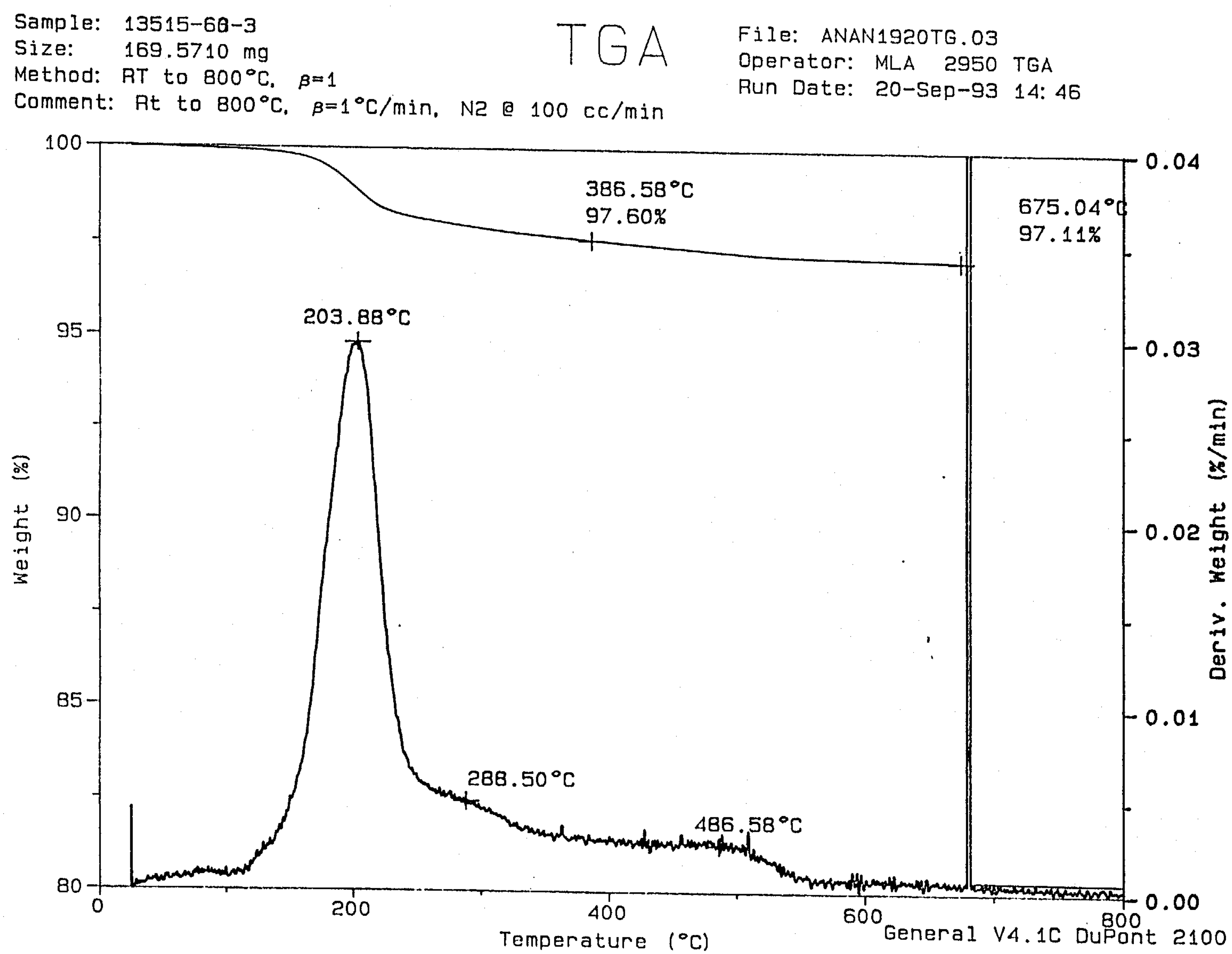
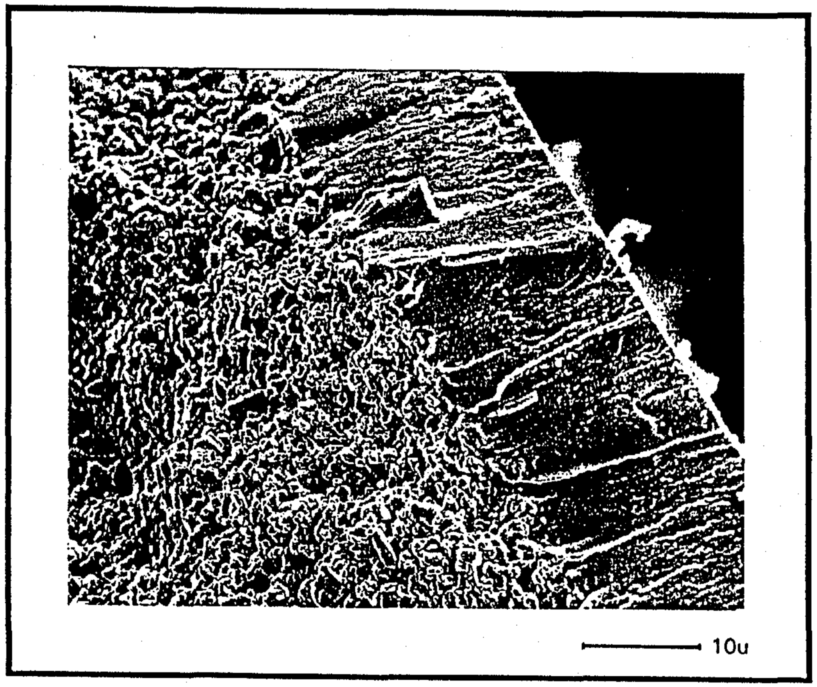
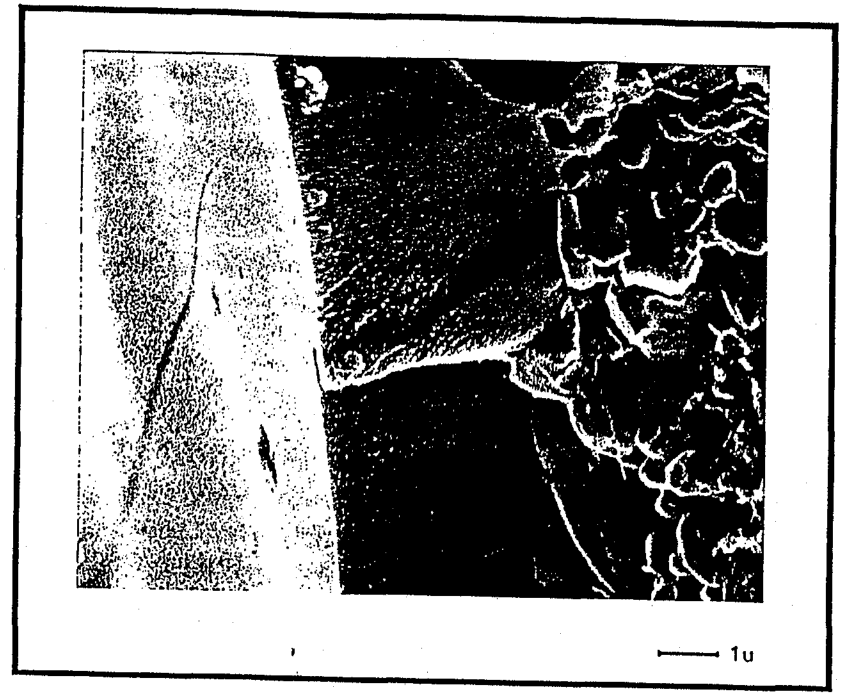


Figure 10. Thermogravimetric Analysis (TGA) of PVDC Coated on Alumina Tube. Note the Various Stages of Mass Loss upto 600 C

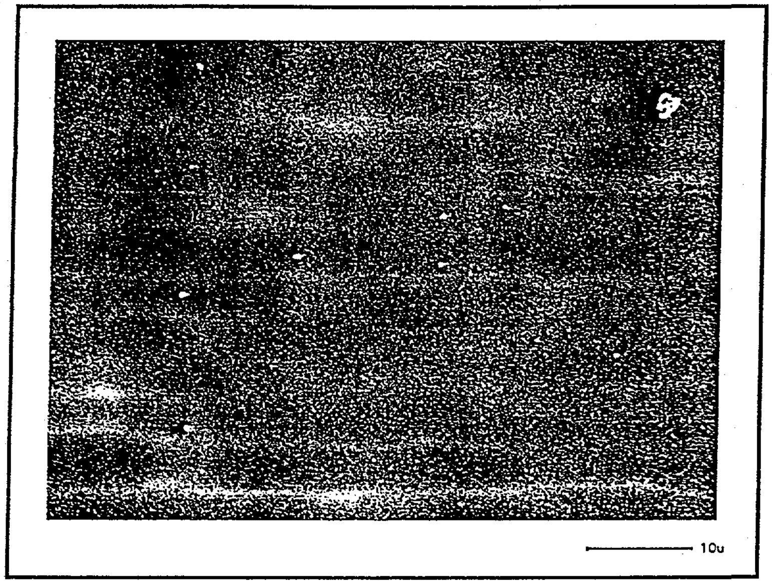


(a)



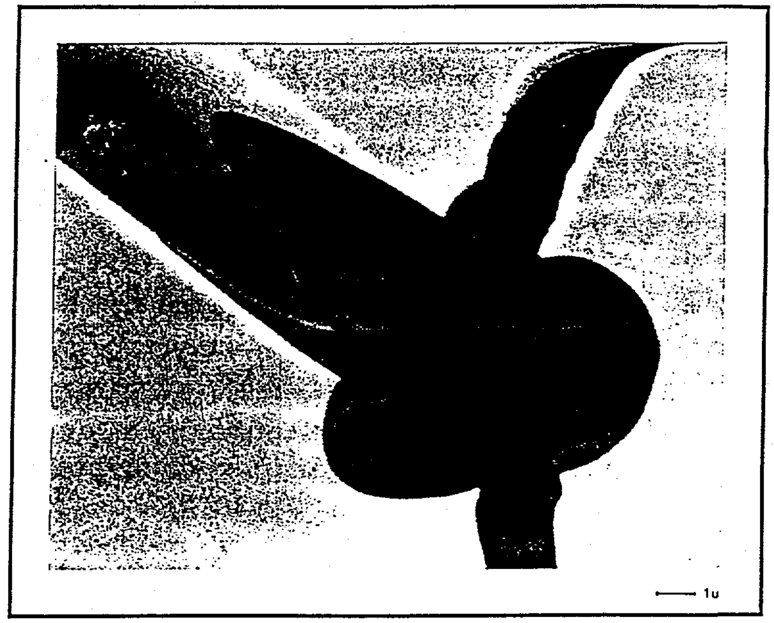
(b)

Figure 11. SEM of PVDC (a) and Carbon (b) Coatings on Alumina



Title 14006-51-5 coated tube Date 02-08-95 Time 14:03
Comment good area MA5151
Mag X2,000 kV 2.0 WD 13mm Spot 7 Scan P3

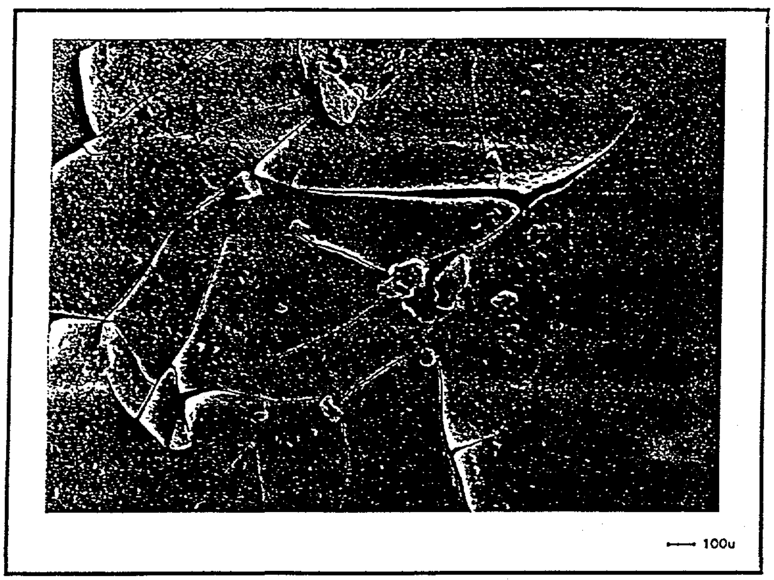
(a)



Title C/alumina post-t 14006-19-6 Date 05-13-94 Time 14:42
Comment inner bore, MA1963
Mag X7,000 kV 5 WD 13mm Spot 5 Scan P3

(b)

(c)



Title 14006-51-4 coated tube Date 02-08-95 Time 13:57
Comment defect area MA5146
Mag X50 kV 2.0 WD 13mm Spot 7 Scan P3

Figure 12. SEMs Showing (a) Smooth Membrane Surface, (b) Bubble in Thick Membrane and (c) Multiple Cracks on Membrane. The cracks and bubbles impart the membrane a matte appearance