See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/231372642

# Effect of the Nature of Different Polymeric Fibers on Steady-State Bed Coalescence of an Oil-in-Water Emulsion

ARTICLE in INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · AUGUST 2004

Impact Factor: 2.59 · DOI: 10.1021/ie049742h

**CITATIONS** READS

22

29

#### 2 AUTHORS:



Radmila M. Šećerov Sokolović

University of Novi Sad

**52** PUBLICATIONS **201** CITATIONS

SEE PROFILE



Slobodan Sokolovic

University of Novi Sad

28 PUBLICATIONS 175 CITATIONS

SEE PROFILE

# Effect of the Nature of Different Polymeric Fibers on Steady-State Bed Coalescence of an Oil-in-Water Emulsion

### Radmila M. Šećerov Sokolović\* and Slobodan M. Sokolović

Faculty of Technology, University of Novi Sad, 21000 Novi Sad, Yugoslavia

The effect of different polymeric fibers on non-Brownian oil drop steady-state bed coalescence was investigated. Three polymeric low-energy smooth fibers were used: polyethylene, polyester, and polyurethane. The oil-in-water system was used as the model of an unstable emulsion, with the drop size smaller than the pore size. Experiments were carried on geometrically similar beds over a wide range of bed permeability (porosity) and a wide range of fluid velocity, from 16 to 70 m  $h^{-1}$ . The bed coalescence efficiency was followed via the effluent oil concentration and critical velocity. The unexpectedly large differences in critical velocities obtained on the investigated materials correlated well with the critical surface tension.

#### Introduction

The separation of finely dispersed liquid—liquid emulsions occurs in various engineering applications, such as the dewatering of petroleum and aviation fuels, prevention of product contamination in liquid—liquid extraction, and removal of dispersed oil and other organics from wastewater prior to its discharge into the recipients, among others.<sup>1</sup>

It is well-known that coalescence of such emulsions can often be induced by flow through a porous medium consisting of either fibrous or granular packing. Fibrous media, which can be made to have both higher porosities and higher specific surface areas than coarse granular media, are observed to give more complete phase separation than granular solids for the same bed depth and operating conditions.<sup>1</sup>

The most relevant properties of a fibrous bed with respect to bed coalescence are morphological and geometrical characteristics including the solid surface size, shape, and arrangement, physical and chemical properties, and heterogeneity.<sup>2,3</sup> The transport of dispersion through a porous matrix is determined by both hydrodynamic action and interfacial interaction between the droplets and collector. However, there have been few studies dealing with the relationship between these two groups of phenomena.<sup>4</sup>

Although bed coalescence has been studied extensively for a long time, there has been no systematic approach to the problem. Experimental conditions differ from study to study, more often in the non-steady-state regime than in the steady-state regime over different fluid orientations. Very often, the chosen experimental conditions did not allow studying the desired phenomenon because of the simultaneous influence of several quantities. The majority of research has been done only at one fluid velocity, so that it is not known whether the system is in the stable or unstable regime. Usually, the bed properties remained insufficiently explained, or were not tackled at all. All this makes it difficult to draw general conclusions from the available data. On the other hand, some investigators tried to draw conclusions

on the basis of poor experimental findings.<sup>5,6</sup> Such a state of affairs is not surprising in view of the great complexity of the process of bed coalescence, as a great many variables come into play.

Sareen et al.<sup>5</sup> have investigated the effect of various bed materials such as cotton, dynel, glass, polyethylene, polypropylene, Teflon, and a mixture of several of them on steady-state coalescence of an oil-in-water emulsion. They varied the fluid velocity from 3.6 to 63 m  $h^{-1}$ , the density of the investigated bed materials from 900 to 2500 kg m<sup>-1</sup>, and the fiber diameter from 8 to 46  $\mu$ m. However, none of the bed properties were given. The authors use the term *closely packed bed*, which is not a measurable quantity when we deal with compressible materials. The majority of conclusions given by the authors are of a general character. A shortcoming of this study is that the experiments were done using a bed of totally unknown properties, whereas the nature, size, and morphology of the fibers were changed simultaneously. Hence, the comparison of the results could not lead to theoretically valid conclusions.

Sharifi and Shaw<sup>6</sup> focused on the issue of fine drop production during drop detachment in the packed-bed coalescers. They investigated various packing materials with different surface properties and shapes: lowenergy surfaces (polypropylene, Teflon, poly(vinyl chloride), polyethylene) and high-energy surfaces (rough and smooth glass, rough and smooth stainless steel, and ceramic). However, as in the above paper, no bed properties (porosity, pore size, etc.) were given. Besides, they used only one very small fluid velocity (10 m  $h^{-1}$ ). As the dispersion flow through the packed bed was vertically upward, the conditions for coalescence on the solid surface were most unfavorable because they lowered the possibility of forming an oil film on the solid surface. Hence, their main conclusions that the maximum size of secondary drops produced on packing surfaces is independent of the nature of the packing material, and that this drop size is expressed as a simple function of the physical properties of dispersion, are quite expectable. However, if we want to study the effect of a solid material, it is necessary to ensure the conditions under which the effect of the solid nature is predominant.

The effect of the chemical nature of the solid surface on bed coalescence has been considered very often only

<sup>\*</sup> To whom correspondence should be addressed. Tel.: +38121450288. Fax: +38121450413. E-mail: radost@uns.ns.ac.yu.

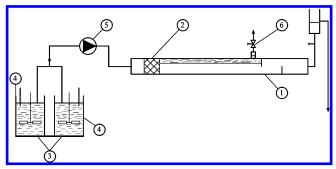


Figure 1. Schematic diagram of the experimental bed coalescer: (1) coalescer body; (2) filter medium; (3) tanks; (4) stainless steel impellers; (5) pump; (6) valve for oil discharge.

on the basis of classification of bed materials into two groups: low-surface-energy and high-surface-energy materials. Thus, solid surface wettability with dispersed liquid was designated as a crucial factor in coalescence phenomena. This statement is illustrated by the following example.

Chieu et al.<sup>7</sup> studied several important variables on non-steady-state and steady-state bed coalescence. Their results showed that oil-wet media were more effective than water-wet media in removing dispersed oil from water. They tested three different fibrous materials (polyester, polypropylene, and glass), using similar bed geometries. They found that polyester and polypropylene felts exhibited a higher efficiency compared to glass, demonstrating thus the importance of the wettability effect. However, the authors did not notice and comment on the significant difference in the efficiency of the two polymeric materials, which is evident from the presented diagrams. As far as we know, nobody has published and pointed out that materials having close values of surface energy can exert a quite different effect on bed coalescence efficiency.

In view of the above the objective of this work was to elucidate whether and to what extent the chemical nature of solid surfaces with similar surface energies can influence the non-Brownian oil drop coalescence in oil-saturated high-porosity media. Hence, we studied coalescence over a wide range of bed properties (porosity, permeability, pore size) and wide range of working velocity using fibers of comparable diameters, for different ratios of pore size to drop size. In this way we have eliminated the noticed shortcomings of the experimental conditions of some other authors.

# **Equipment and Operating Procedure**

The experiments were performed on a laboratoryscale bed coalescer, consisting of two sections, a bed and a settling section (1, 2), Figure 1. The fluid flow orientation was horizontal (H) through the bed. The emulsion was prepared in two tanks (3), by continuous stirring of the contents with a stainless steel impeller (4). The emulsion was continuously forced by a membrane dosage pump. The settled oil was discharged discontinuously through the valve (6). The experiments were carried out in a steady-state regime, which was achieved by preoiling the fibers. In this way, a steady state was established from the very beginning of the experiment, which was confirmed by monitoring the pressure drop, which did not change with time.

The experimental bed was formed of closely packed compressible polymeric fibers. Three different polymer materials were investigated: polyethylene (BA), poly-

ester (PE), and polyurethane (PU). The microstructure and surface morphology of the fibers were characterized by scanning electron microscopy (SEM). The pore diameter for different bed bulk densities was checked by optical microscopy. Experiments were realized in a broad range of bed properties.

The length of each experimental bed was constant, 5 cm. In one experiment the bed permeability was kept constant, using five values of bed permeability. The bed permeability,  $K_0$ , was calculated from the measured pressure drop across the bed for tap water, and the data complied with Darcy's law. The porosity of the bed was measured by the weighing method.

In our previous study of the effect of variable bed permeability, we arrived at the conclusion that the separation efficiency is highly influenced by the bed permeability (porosity) only over a specific range, bordered by the quantity that we call the critical permeability. The region below the critical permeability brings about the instability of the system, with low and unpredictable efficiency. Hence, it would be necessary to determine the value of the bed critical permeability for each material and work with a bed of higher permeability to obtain optimal separation conditions.8

Velocities of 16-70 m  $h^{-1}$  for the constant oil-in-water emulsion and constant mean drop diameter were applied. A selected velocity was kept constant for 1 h, and composite samples were taken in the last 15 min in 5 min intervals. The working temperature was constant, 20 °C. The inlet mean droplet diameter of about 20  $\mu$ m was proved with use of an optical microscope.

A naphthenic-base vacuum fraction, through boiling point 350–400 °C, was used as the dispersed phase. The main characteristics of the oil were a density at 20 °C of 844.73 kg m<sup>-3</sup>, a mean molar mass of 349 g mol<sup>-1</sup>, a viscosity at 35 °C of 21.73 mPa s, a neutralization number of 0.229 mg of KOH  $L^{-1}$ , a pour point of -30°C, a surface tension of 27.15 mN m<sup>-1</sup>, and an interfacial tension of 18.04 mN m<sup>-1</sup>. The surface tension was measured with use of a stalagmometer, and the interfacial tension with use of a spinning drop interfacial tensiometer, model 500 Corexport.

The oil concentration in the effluent was determined by IR spectrometry from a carbon tetrachloride extract, after addition of HCl to obtain pH 2, to stabilize the oily water samples.

#### **Results and Discussion**

**Properties of the Fibrous Materials and Their Bed.** It is known that the ratio of the critical surface tension of a solid to the liquid surface tension determines the character of solid wettability. On the basis of the critical tension, solid materials were classified into two groups:10 low-energy materials and high-energy materials. All our bed materials belonged to the former group.

The critical surface tension is intimately related to the chemical surface composition. Even small changes in the outermost atomic layer are reflected in a change of the critical surface tension. The critical surface tension for polyethylene is  $31 \text{ mN m}^{-1}$ , for polyester it is 43 mN m<sup>-1</sup>, and for polyurethane it is 23 mN m<sup>-1</sup>. A common characteristic of the investigated materials is their good wettability with the dispersion phase (surface tension  $27.15 \text{ mN m}^{-1}$ ).

On the other hand, it is well-known that only geometrically similar fibrous beds can yield equal oil



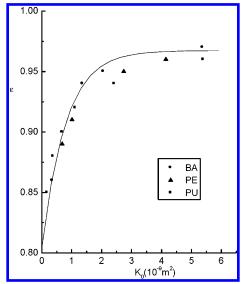


Figure 2. Dependence of porosity on bed permeability.

**Table 1. Characteristics of Bed Materials** 

material	$^{ ho,}_{ m kg~m^{-3}}$	$d_{ m f}$ , $\mu{ m m}$	$\epsilon$	φ	$_{10^{-9} \text{ m}^2}^{K_0,}$	$D_{ m p}$ , $\mu{ m m}$	$D_{ m p}/d_{ m d}$
BA	930	40	0.97	0.03	5.37	500	25
			0.95	0.05	2.06	450	22
			0.94	0.06	1.36	400	20
			0.90	0.10	0.68	300	15
			0.86	0.14	0.35	250	12
$\mathbf{PE}$	1400	60	0.96	0.02	4.15	600	30
			0.95	0.05	2.74	400	20
			0.91	0.09	1.01	300	15
			0.89	0.11	0.68	200	10
PU	1200	50	0.96	0.04	5.39	500	25
			0.94	0.06	2.42	400	20
			0.92	0.08	1.12	300	15
			0.88	0.12	0.38	250	12
			0.85	0.15	0.18	200	10

saturations. 11 Hence, it is very important to ensure in steady-state bed coalescence equal amounts of oil in the bed, to create the conditions for a dominant effect of the nature of the fibrous material.

Furthermore, we used different polymeric fibers of similar diameters and smooth surfaces, to obtain similar bed geometries in a broad range of bed properties, permeability ((5.39–0.18)  $\times$  10<sup>-3</sup> mm<sup>2</sup>), porosity (0.97– 0.85), and solid surface (3.00-12.00 mm<sup>-1</sup>), over the same ratio of pore size to drop size (25-10) (Table 1).

As we pointed out in our previous paper concerning polyurethane, 6 the relationship between the bed porosity and bed permeability is the best evidence for the bed geometrical similarity. Figure 2 shows that the same holds for the other two materials-polyethylene and

**Oil-in-Water Steady-State Bed Coalescence.** The bed coalescence efficiency was followed via the effluent oil concentration ( $C_e$ ) and critical velocity ( $V_{k15}$ ). The critical velocity was determined from the exponential dependence of the effluent oil concentration on the fluid velocity, in each particular experiment. In our studies, the critical velocity  $(v_{k15})^8$  is the fluid velocity determined at a point when the effluent oil concentration reaches 15 mg  $L^{-1}$ , this concentration often being quoted as the tolerable level in oily water. As the working velocity is a crucial factor for equipment size and capital costs, the goal of optimization is to find the conditions corresponding to its maximum, which must be below the critical velocity.

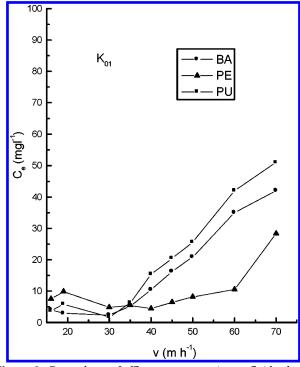


Figure 3. Dependence of effluent concentration on fluid velocity for PU, BA, and PE at the bed permeability  $K_{01}$ .

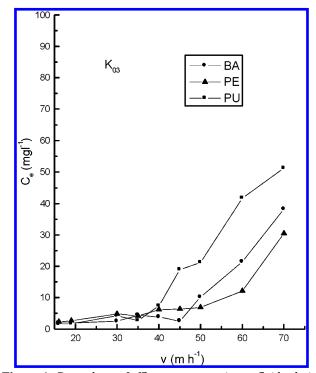


Figure 4. Dependence of effluent concentration on fluid velocity for PU, BA, and PE at the bed permeability  $K_{03}$ .

Some typical results for the effluent oil concentration over all applied velocities are given in Figures 3 and 4. Results were obtained for bed permeabilities  $K_{01}$  and  $K_{03}$ , respectively. As can be seen, the effluent oil concentration reached a value of 15 mg  $L^{-1}$  first for PU, after that for BA, and finally for PE. As can be seen from our results, the extent of the interaction of the fibrous material and dispersed phase should be measured in the range of critical fluid velocity corresponding to the moment when the hydrodynamic force becomes dominant, i.e., exceeding the adhesive force. The physi-

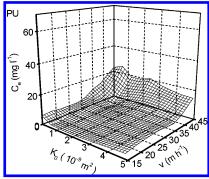


Figure 5. Three-dimensional diagram representing the interdependence of effluent oil concentration, bed permeability, and fluid velocity for PU.

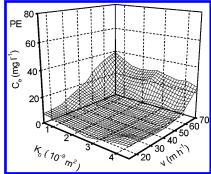


Figure 6. Three-dimensional diagram representing the interdependence of effluent oil concentration, bed permeability, and fluid velocity for PE.

cal perturbation increasing the fluid velocity promotes oil globule detachment from the solid surface. The existing phenomenon explains the exponential dependence of the effluent oil concentration on the fluid velocity.

Similar to the findings of some other authors, 6 the effluent oil concentration was independent of the chemical nature of the bed material in the range of small fluid velocities. As already mentioned, in steady-state bed coalescence over the range of the velocity below the critical velocity, the solid surface is covered with oil, and newly coming droplets are much more readily attached to the covered oily surface than the bare solid surface.

In view of the above, three-dimensional diagrams give a much better picture of the interdependence of the broad ranges of bed permeability and fluid velocity on the effluent concentration. Figures 5 and 6 give such relationships for polyurethane and polyester, respectively. As can be seen, the forms of the diagrams are generally similar, the difference being only in the value of the fluid velocity corresponding to the break point. These results, obtained for several materials, support our previous recommendation8 that the critical velocity should be used in the analysis of bed coalescence phenomena, as it is a more sensitive parameter than the previously used effluent concentration or efficiency.

The above is straightforward if we look at the diagrams presented in Figures 7-9. Figure 7 illustrates the dependence of the critical velocity on the bed permeability for the three investigated materials. Evidently, the existence of the critical permeability, previously found for polyurethane,8 has been confirmed for the other two materials. Therefore, it is clear that the experiments carried out below the critical bed permeability cannot lead to valid conclusions. Namely, the differences between different materials can be seen only

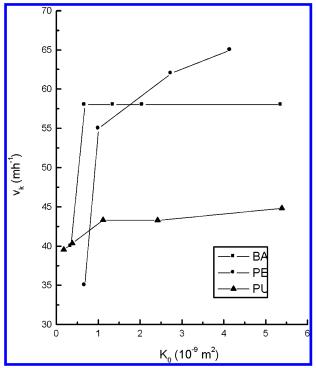


Figure 7. Dependence of critical velocity on bed permeability for the investigated polymer beds.

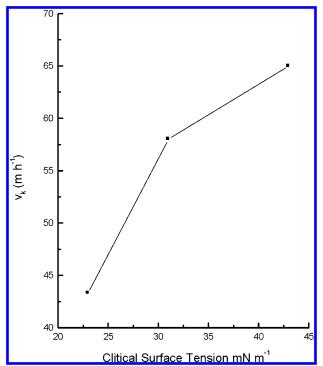


Figure 8. Dependence of critical velocity on critical surface tension.

in the range following the break point, corresponding to the critical bed permeability. This value can also be determined on the basis of Figure 2 ( $K_0 > 1.5 \times 10^{-9}$ m2), when the bed porosity becomes independent of a further increase of the bed permeability. The given range corresponds to the ratio of the pore size to the drop size,  $D_{\rm p}/d_{\rm d} \geq 20$ .

A low bed permeability corresponds to a smaller pore size, Table 1, and fewer interconnected pores available for fluid flow, drastically increasing the interstitial velocity at the same overall working velocity. So, even

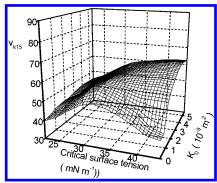


Figure 9. Three-dimensional diagram representing the interdependence of critical fluid velocity, critical surface tension, and bed permeability.

at a low working velocity, high local velocities contribute to the pronounced influence of hydraulic forces and therefore low coalescence efficiency. A high interstitial velocity contributes to a lower drop capture probability, decreasing the capture time.

As can be seen from Figure 7, the values of the critical velocity corresponding to the conditions above the critical bed permeability are for PU 45 m h<sup>-1</sup>, for BA 55 m  $h^{-1}$ , and for PE 65 m  $h^{-1}$ . It is very important to point out that although all three solid surfaces belong to low-energy materials, well wetted with dispersed liquid, they have very different critical velocities over similar working conditions. Bearing in mind that the adhesion force depends at the same time on the chemical nature of the solid surface and the chemical nature of the dispersed and continuous phase, it is straightforward that the proper choice of the bed material can be made only on the basis of experiments carried out for the given liquid—liquid system.

A question arises as to how to explain the observed unexpected differences between the above numerical values of critical velocities for the investigated materials. Certainly, this is a very complex issue involving a number of macroscopic parameters such as bed geometry, fluid velocity, and solid surface properties and surface phenomena, including adhesion, capillarity, surface and interface tension, and wetting. Hence, a correlation should be sought between measurable quantities—bed coalescence variables—and some surface phenomena. As the critical velocity is the most important bed coalescence variable, we chose to investigate the possible correlations. On the other hand, the critical surface tension is the quantity reflecting the mutual interaction of the solid and the two-liquid emulsion. Hence, we considered it appropriate to check whether there was an interdependence of these two quantities.

Thus, in Figure 8 we relate the critical surface tension to the critical velocity. It is evident that correlation between two chosen variables exists for the investigated bed material. Polymeric fibers with the highest critical surface tension allow maximal critical velocity or maximal working velocity. For our circumstances it is for PE. On the basis of these results it can be asked whether the critical surface tension represents a measure of the intensity of adhesion force within the low-energy materials.

In Figure 9 is illustrated the effect of introducing into play another important variable, i.e., bed permeability. The given diagram confirms that the system behaves differently at lower and higher values of the bed permeability. The dependence of the critical velocity differs below and above the critical bed permeability. It is evident that for the optimal range of the bed permeability the critical velocity increases with an increase in critical surface tension.

Namely, in view of the existence of different chemical groups present on both the solid surface and dispersed phase, a difference in the intensity of their interaction could be expected. Hence, it is questionable whether the obtained great differences in our results could be explained only in terms of van der Waals forces.

#### Conclusion

Although all the investigated materials belong to lowenergy solids, commonly used in dispersed oil separation, we found that they exhibited a marked difference in bed coalescence efficiency. As this parameter is influenced by a number of surface phenomena such as adhesion, capillarity, surface tension, and wetting, a correlation should be sought between these phenomena and measurable quantities, bed coalescence variables. Our results showed that the critical velocity best meets this purpose. For the optimal range of bed permeability, the critical velocity increases with an increase in the critical surface tension.

The observed differences between the investigated materials in the interaction with the chosen dispersed phase could hardly be explained only in terms of the difference in van der Waals force intensity.

The presented results give rise to some new issues in directing further studies in this domain. The question of whether the change of the nature of the oil phase would essentially influence the relationship between the critical velocities for the same solid materials remains to be answered.

# Acknowledgment

This work was supported by the Ministry of Science, Technologies and Development of the Republic of Serbia.

#### **Nomenclature**

 $D_{\rm p} = {\rm channel\ diameter,\ } \mu{\rm m}$ 

 $d_{\rm f}$  = fiber diameter,  $\mu$ m

 $d_{\rm d} = {\rm mean\ drop\ diameter},\, \mu{\rm m}$ 

 $K_0 = \text{bed permeability, m}^2$ 

 $K_{0k}$  = critical bed permeability, m<sup>2</sup>

 $S = \text{solid surface, mm}^{-1}$ 

Greek Letters

 $\epsilon = \text{bed porosity}$ 

 $\phi$  = fraction of solid

 $\rho$  = fiber density

## **Literature Cited**

- (1) Spielman, L. A.; Su, Y. P. Coalescence of Oil-in-Water Suspensions by Flow through Porous Media. Ind. Eng. Chem. Fundam. 1977, 16, 272-282.
- (2) Ryan, J. N.; Elimelech, M. Review: Colloid Mobilization and Transport in Groundwater. Colloids Surf., A 1996, 107, 1–56.
- (3) Sung-Jae, Kim.; Benefield, L. D. Physicochemical Factors Influencing Colloidal Particle Transport in Porous Media. Sep. Sci. Technol. 1996, 31(19), 2621-2653.
- (4) Maini, B.; Wassmuth, F.; Schramm, L. L. Fines Migration in Petroleum Reservoirs. *Adv. Chem. Ser.* **1996**, *251*, 321–375.
- (5) Sareen, S. S.; Rose, P. M.; Gudesen, R. C.; Kintner, R. C. Coalescence in Fibrous Beds. AIChE J. 1966, 12 (6), 1045.

- (6) Sharifi, H.; Shaw, J. M. Secondary Drop Production in
- Packed-Bed Coalescers. *Chem. Eng. Sci.* **1996**, *51* (21), 4817–4826. (7) Chieu, J. N.; Gloyna, E. F.; Schechter, R. S. Device for Evaluating Coalescence of Oil Emulsions. J. Environ. Eng. 1977, April, 163-175.
- (8) Šećerov Sokolović, R.; Sokolović, S.; Vulić, T.; Marinković Nedučin, R. Effect of Fibrous Bed Permeability on Steady-State Coalescence. Ind. Eng. Chem. Res. 2003, 42 (13), 3098-3102.
- (9) Šecerovć Sokolović, R. M.; Sokolović, S. M.; Đoković, B. D. Effect of Working Conditions on Bed Coalescence of an Oil-in-Water Emulsion Using a Polyurethane Foam Bed. Ind. Eng. Chem. Res. 1997, 36 (11), 4949-4953.
- (10) Berg, J. C. Wettability; Surfactant Science Series 49; Marcel Dekker: New York, 1993; p 157
- (11) Spielman, L. A.; Su, Y. P. Coalescence of Oil-in-Water Suspensions by Flow through Porous Media. *Ind. Eng. Chem. Fundam.* **1977**, *16* (2), 272–282.

Received for review April 1, 2004 Revised manuscript received June 16, 2004 Accepted July 16, 2004

IE049742H