Characterization of Ultrafiltration for Flexographic Newsprint Deinking

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The presence of flexographic printed newspapers in the furnish to a recycling/deinking plant results in lowered brightness of the secondary fiber product. This is due to the surface chemistry of flexographic pigment particles, which are hydrophilic and therefore not removed by conventional flotation deinking. Although washing effectively removes flexographic pigment particles from fiber suspensions, the resulting filtrate will contain substantial quantities of pigment necessitating clarification prior to recycling this water to the process or discharging it to the environment. Conventional effluent treatment (dissolved air flotation) is not capable of removing these hydrophilic particles effectively, even with the addition of large amounts of collector chemicals. Ultrafiltration has been demonstrated to be a viable technique for the removal of flexographic pigments from aqueous dispersions. This paper describes the results of a statistically designed experimental sequence tailored to optimize the ultrafiltration process for clarifying flexographic pigment dispersions. Important operational parameters investigated include temperature, pigment concentration, surfactant concentration, and membrane pore size. Interactions between the variables were investigated. Efficiency of the ultrafiltration process was assessed in terms of permeate flux

Newsprint printed with water-based flexographic inks presents unique challenges to the deinking operation. Acrylic polymers used as binder resins in flexographic ink formulations cause the pigment particles to be hydrophilic, and thus form colloidal dispersions of very fine particles of less than five microns in diameter[1,2] during pulping under alkaline conditions. The resulting small hydrophilic particles do not contact and adhere to the rising air hubbies in froth flotation, and therefore remain in the pulp suspension leaving the flotation operation[3]. The inclusion of these flexographic pigments in the deinked pulp produces a drastic reduction in brightness[1].

Modifications to froth flotation have been proposed to make this operation more efficient at removing flexographic pigments from secondary fiber suspensions. Polymeric collectors and flocculants can be added to the fiber suspension prior to the flotation operation. This technique is aimed at agglomerating the flexographic pigment particles into a larger, more hydrophobic assemblage which would then be more amenable to removal by froth flotations. The drawback to this approach is the addition of chemicals, which represents increased operational expenses for the deinking plant, and makes process control more difficult. Another approach is to perform a two stage deinking operation in which the ONP furnish is pulped under neutral or acidic conditions[6]. Pulping at low pH prevents the acrylic binder resins in the flexo ink from becoming ionized, resulting in the formation of larger more hydrophobic agglomerations of flexo pigments in the pulper. This fosters a greater driving force for the flexo ink particles to attach to air bubbles in the first froth flotation operation, also performed under neutral or acidic conditions. Although pulping and flotation at low pH is beneficial to flexographic deinking, the oil-based inks used in letterpress and offset printing would not be efficiently removed under these conditions, necessitating a second deinking cycle at alkaline conditions[6]. This approach has demonstrated successful results in deinking a mixed furnish containing ONP printed with oil-based and water-based inks. However, the process requires two flotation operations and additional dewatering and clarification capabilities between the acid and alkaline loops, representing a significant capital expenditure and higher operational costs, which have so far been barriers to implementation.

The physical and chemical properties of flexographic pigment particles lends them to efficient removal by washing techniques[7], However, the wash filtrate containing the flexographic pigments cannot be directly recycled to the process without reducing the brightness of the product pulp. Nor can the pigment laden filtrate

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be discharged to the environment. For these reasons the wash filtrate must be clarified of the flexographic pigment, which remains a significant problem, Dissolved air flotation (DAF) clarification has not been shown capable of completely removing hydrophilic flexographic pigments from wash filtrate even with the addition of significant quantities of cationic collectors and anionic flocculants[8].

Membrane separation technology is a potentially viable method for the clarification of flexographic pigment dispersions from wash filtrate[9]. Membrane filtration removes contaminants based on size. There are three primary membrane filtration techniques: reverse osmosis, ultrafiltration, and microfiltration. These techniques differ mainly in the pore size of the membrane, and thus the cutoff size of materials which are retained. Reverse osmosis (RO) membranes have the smallest pores, and can be designed to retain all components, dissolved and suspended, passing only the solvent. RO is typically used for water purification and desalination. Ultrafiltration (UF) membranes have larger pores, and allow small dissolved molecules to pass, retaining larger (higher molecular weight) solutes and suspended particles. Microfiltration (MF) membranes have still larger pores, and typically allow any dissolved components to permeate through the membrane while retaining suspended solid materials.

Most modem membrane separation processes are operated under “cross-flow” conditions[10]. The membrane is configured in a tubular or hollow fiber geometry, in which the liquid to be processed flows axially through the interior of the tube under pressure. The pressure forces any permeable materials to pass through the membrane, while retained species remain in the feedstream. The permeation rate of fluid through the membrane is reported as flux, defined as the volume of permeate produced per unit of membrane surface area per unit time (typically in units of $L/m^2 hr$). As fluid passes through the membrane, retained material is brought to the membrane surface by convective transport. This causes a concentration gradient to be formed in the radial direction, which is known as the concentration boundary layer[11]. The buildup of retained material in the region of the membrane surface is balanced by the diffusion of these materials back into the bulk fluid where the concentration is lower. The axial flow of fluid through the tube creates a shear stress field parallel to the membrane surface which increases the rate of back-diffusion into the bulk fluid stream. The cross-flow configuration prevents extensive "blinding" of the membrane, facilitating high flux and extended filtration times.

Earlier work at Auburn has demonstrated that ultrafiltration and microfiltration are both capable of completely removing flexographic pigment from aqueous dispersions typical oft hose formed by wash deinking of newsprint[12]. Moreover, it was found that ultrafiltration can operate at higher sustained flux levels at most ink concentrations of interest, and is therefore a better choice than microfiltration for clarifying flexographic ink dispersions[13]. A proposed scheme for the application of ultrafiltration techniques in a deinking process is shown in Figure 1. Deinking a mixed secondary newsprint stock containing both oil-based and water-based inks can be accomplished with a combination of flotation and washing operations. The resulting filtrate would be clarified of water dispersible **pigments** using a multiple stage ultrafiltration operation prior to being recycled to the process. The concentrated ink residue could possibly be utilized in energy recovery. The number of stages, membrane surface area of each stage, operating conditions, and location in the process at which to apply ultrafiltration must be optimized in order to maximize production rate and useful membrane lifetime while minimizing capital (membrane) and pumping costs.

A primary goal of this phase of research was to develop an understanding of the importance of several operating variables on the performance of ultrafiltration in clarifying flexographic ink dispersions. This paper describes the results of a statistically designed experimental sequence which was employed to develop a mathematical model capable of predicting the optimum conditions at which to operate the ultrafiltration process for clarifying these dispersions. Operational parameters investigated include temperature, pigment concentration, surfactant concentration, and membrane pore size. Interactions between the variables were investigated. Efficiency of the ultrafiltration process was assessed in terms of permeate flux.

EXPERIMENTAL

The polysulfone hollow fiber ultrafiltration membranes used in this study were constructed in modules of 1 ft^2 surface area in shell and tube configurations consisting of 68 hollow fibers of 0.043

inch (0.109 cm) ID. The molecular weight cut off (MWCO) of a UF membrane is a measure of its pore size, or retention ability, and is the approximate molecular weight of the smallest compound retained. Three UF membranes of differing MWCO (10,000, 50,000, and 500,000) were used. The experimental apparatus was equipped with adequate instrumentation and controls to manipulate pressure drop across the membrane surface (transmembrane pressure or ΔP_{tm}), temperature, and flowrate through the membrane module (Figure 2).

Feed solutions for UF experiments were prepared from tap water, flexographic ink, and a commercially available anionic and nonionic surfactant mixture. These solutions represent an ideal case of de-inking wash filtrate, with no other contaminants such as fines present. Sodium hydroxide was used to adjust the pH to 10. Ink concentrations ranged from 0.12% to 12.9% , as determined by visible light spectroscopy[14]. Surfactant was added in varying amount to form solutions ranging from 0 to 1% ADDED surfactant. It is important to realize that the ink used to form the experimental feedstreams contained several surface active materials. The amount of added surfactant discussed in this paper refers to the amount of commercial surfactant which was added to the feedstream independent of the surface active materials already present in the ink. The shear forces associated with the cross-flow rate of feed across the membrane surface strongly affects the formation of a pigment filter cake (gel layer) on the membrane surface, which in turn affects flux. A cross-flow rate of 1.0 gpm was maintained during all UF experiments. This flow rate was found adequate to prevent excessive gel formation[15],

The experimental procedure was as follows. The UF module to be used and the tank containing the ink dispersion to be filtered were connected to the apparatus. While the UF module was valved off, the recirculation pump was turned on and recirculation begun. A 3000W in-line heater was used to bring the feedstream up to the desired temperature (30, 40, or 50°C). When this temperature was achieved the heater was turned off and temperature held constant using a water bath. A cooling water loop was required in the water bath during the 30°C experiments in order to remove heat from the system. At this point flow was introduced through the UF module and two metering ball valves were used to maintain the desired operating conditions of 25 psi ΔP_{tm} and 1 gpm cross-flow rate. Pigment concentration remained constant as permeate was returned to the feed tank, Flux was measured by the timed collection of permeate in a tared beaker which rested on a balance (the specific gravity of the permeate was determined to be 1.0). After the flux measurement, collected permeate was returned to the feed tank. Flux was measured at approximate ten minute intervals for the duration of the experiment, which ranged from 90 to 140 minutes depending on the stability of the flux measurements. The results of the experiment were reduced to a single data point, that being the average of the flux measurements taken within the time interval 80-100 minutes. At least two flux measurements (typically three or four) were used in obtaining this average.

A total of 42 experiments of this nature were performed at different levels of the four control variables (ink concentration, temperature, amount of added surfactant, and UF membrane MWCO). The first three of these variables are continuous in nature, while membrane MWCO is a categorical variable (it exists at three discrete levels only: 10,000, 50,000, and 500,000). The combinations and levels of the variables were determined in a statistical manner in order to most efficiently fill the experimental sample space with the minimum number of experimental trials. The experiments were performed in random order to negate the effects of any extraneous parameters which were not accounted for. Five of the 42 experiments were replicates and were first used to estimate the reproducibility of the results. A mathematical model was developed from the data to characterize flux as a function of the four control variables. The data from the five replicate experiments were considered as unique and used in the formulation of this model. This technique allowed the accumulation of useful information regarding the influence of operational parameters on ultrafiltration performance from a limited amount of data.

Immediately following each experiment the membrane modules and entire flow path were rinsed with tap water. A 0.5% surfactant solution (with pH adjusted to 10) was then pumped through the membrane module and associated piping for five minutes at low pressure and high flow rate (10 psi, >2 gpm). The dirty cleaning liquid was drained from the system, and a fresh cleaning solution was recirculated for an additional five minutes. A third cleaning was performed in the same manner with a fresh cleaning solution. A final cleaning solution was prepared and

recirculated through the UF module at the experimental conditions of 25 psi ΔP_{tm}, 30°C and 1.0 gpm. The duration of this cleaning was extended for at least 50 minutes, with flux of the cleaning solution being measured at ten minute internals. This data can be used to evaluate the effectiveness of the cleaning procedure on restoring membrane performance.

RESULTS

Figure 3 shows a plot of flux vs. time for a typical experiment. This data was collected whale processing a 0.11% ink concentration dispersion with 0.5% added surfactant using a 50,000 MWCO membrane at 50°C. The permeate was determined to be pigment free by visible light spectrophotometry[14]. Flux decreased rapidly at first, then approached a relatively stable level within 15 minutes. Similar plots were constructed from data collected during each of the 42 experiments. From each plot a flux value was obtained corresponding to the steady state flux of that particular membrane at those operating conditions. For example, from the data displayed in Figure 3 flux values observed after 82,92, and 102 minutes of operation were averaged to give a single flux estimate of 82 L/m^2hr.

A quadratic polynomial model was fit to these data and used to approximate the response of flux as a function of the four control variables temperature, ink concentration, amount of added surfactant and membrane MWCO. Ink concentration was transformed to a log scale because previous results have shown the relationship between flux and ink concentration to be exponential[15]. The coefficients of the model were calculated using a least squares algorithm. Because membrane MWCO is a categorical variable it was handled differently than the three continuous variables. Values of membrane MWCO cannot be interpolated, therefore differences were calculated between levels to model this term[16]. The coefficients were modified from one level to the next by accounting for the main effect contrasts between levels of MWC0[17].

Of the three continuous variables, ink concentration had the greatest effect on flux. Figure 4 shows the model generated response surface for flux as a function of % surfactant and ink concentration at 50°C using the 10,000 MWCO membrane. At concentrations above 0.3% ink (corresponding to $\log_{10}$(ink) greater than -0.5) there was a direct relationship observed between flux and log of ink concentration, corroborating earlier results which indicated that flux falls exponentially with increasing ink concentration[15] At lower levels ink concentration had little effect on flux.

Figure 5 shows the same response surface with the actual flux data points included and the angle of view rotated to more clearly see the quality of the model. Although data from all 42 experiments were used in formulating the model, only seven observations were applicable for display on this plot at these experimental conditions. In this view the effect of ink concentration on flux is clear. Figures 6 and 7 show similar flux predictions and data collected at a lower temperature (30°C) using an ultrafiltration membrane with 500,000 MWCO. An approximate exponential decrease in flux with increasing ink concentration was again observed.

Temperature was the second most influential of the variables. Operating at elevated temperatures resulted in increased permeation rates. The predicted flux response using the 10,000 MWCO membrane to process ink dispersions with no added surfactant is shown in Figure 8. In Figure 9 data collected from individual experiments under applicable conditions is show and the angle of view rotated to more clearly show the fit of the model to data. The beneficial effect of temperature on permeation rates when using this membrane at low surfactant levels can be observed in this figure. Temperature has less of an effect on flux when using the 500,000 MWCO membrane, in which the pores are larger (Figure 10). This indicates that the effect of temperature is possibly due to its influence on the viscosity of the "solvent", in this case water and dissolved low molecular weight materials present in the ink dispersion. Since the 10,000 and 50,000 MWCO membranes have smaller pores than the 500,000 MWCO membrane, viscosity has a greater effect on flux and therefore temperature was a more influential factor.

An interesting interaction between surfactant level and temperature was observed, as shown by the predicted response of permeation rate when processing ink dispersions with the 10,000 MWCO membrane (Figure 11). At low temperatures, increasing the surfactant concentration boosted permeation rates, whereas at higher temperatures adding surfactant had an opposite effect. Similarly at high surfactant levels (1% added surfactant) increasing the temperature reduced permeation rates, in contrast to the beneficial effects of elevated temperature when no surfactant was

added. The interaction between temperature and surfactant was most evident at high ink concentrations

The nature of the temperature-surfactant interaction appeared to be different when using the 500,000 MWCO membrane (Figure 12). Neither temperature nor surfactant concentration were as strongly influential on flux as when using the 10,000 or 50,000 MWCO membranes. The optimum flux with the 500,000 MWCO membrane was achieved at intermediate levels of both temperature and surfactant rather than at the extremes of these variables.

In general it is expected that membranes with larger pores will allow higher permeability, and therefore higher flux rates provided that the larger pore size does not result in increased fouling due to entrapment of particles in the pore opening area. As can be seen in Figure 13, the 500,000 MWCO membrane performed equal to or better than the 10,000 or 50,000 MWCO membranes under most operating conditions. However, when no surfactant was added to the feed the 500,000 MWCO membrane did not always produce higher permeation rates than the other membranes, which indicates that surfactant addition may reduce pore blockage when using the 500,000 MWCO membrane. The smaller pore size of the 10,000 and 50,000 MWCO membranes should impede the entrance of pigment particles into the pores, allowing these membranes to be more resistant to this type of fouling, even without surfactant addition.

CONCLUSIONS

To summarize the results of this study, several important conclusions can be made:

1) Flexographic pigments were completely removed by ultrafiltration producing pigment free permeate.

2) Ink concentration was the most influential variable studied. Increasing ink concentrations decreased permeation rates. This effect became less significant at ink concentrations below 0.3%.

3) Operating at elevated temperature increased permeation rates when membrane pore size was small (10,000 & 50,000 *MWCO)*. Temperature was less influential when using the 500,000 MWCO membrane.

4) Adding surfactant enhanced permeation rates when operating at low temperature and decreased permeation rates at high temperature. This was most evident when processing high ink concentration dispersions, and least noticeable when using the 500,000 *MWCO* membrane.

LITERATURE CITED:

1. **Mah, T., Reid, F., Yau, T.**, "Deinking of Flexographic Ink by Flotation Process", CPPA Annual Meeting Preprints, Vol 79A: 119-128 (Jan 26-29, 1993).

2. **Rangamannar, G., Grube, G., Karneth, A. M.**, "Flexographic Newsprint Deinking", Proceedings, 1992 International Printing & Graphic Arts Conference, p. 363 (1992).

3. **Putz, H.J., Schaffrath, H.J., Göttsching, L.**, "Deinking of Oil- and Water-Borne Printing Inks: A New Flotation De-inking Model", Pulp & Paper Canada 94:7(1993).

4. **Liphard, M., Schreck, B., Hornfeck, K.**, "Interfacial Studies and Application Tests on the Flotation of Printing Inks and Fillers", 1990 TAPPI Pulping Conference Proceedings, pp. 965-973.

5. **Fedrigon, A.**, "Wastewater Treatment and Disposal of Water Based Flexographic Inks", International Paper Board Industry, 34:7(28-31), (July 1991).

6. **Galland, G., Vernac, Y.**, "Deinking of Wastewater Containing Water-Based Flexo-Printed Newsprint", Pulp & Paper Canada 94(6):71, (1993).

7. **Wallström, E.**, "Water-Borne Flexo for Newspaper Printing", Advances in Printing Science and Technology, 19, chap. 14:199-210, (1988).

8. **Tremont, S.R.**, "Impact of Neutral Deinking Chemistry on DAF Clarification and Sludge Dewatering of Deink Plant Rejects", 1993 TAPPI Pulping Conference Proceedings, p.749, (1993).

9. **Skelton, R.**, "Experiences in the [United] States with Ultrafiltration for Treatment of Aqueous Flexographic Ink and Starch Wastes in the Corrugated Container Industry", Converter, 22(4):14, 17-18, (1985).

10. **Forbes, F.**, "Considerations in the Optimization of Ultrafiltration", The Chemical Engineer, January, 1972, p.29 (1972).

11. **Cheryan, M.**, "Ultrafiltration Handbook", Technomic Publishing Co., Lancaster, PA, p.74, (1986).

12. **Upton, B.H., Krishnagopalan, G.A.**, "Deinking of Flexographic Newsprint: Membrane Filtration as a Method of Wash Filtrate Clarification", AIChE 1994 Spring National Meeting, April 17-21, Atlanta, GA, (1994).

13. **Upton, B.H., Krishnagopalan, A., Abubakr, S.**, "Flexographic Newsprint Deinking: Wash Filtrate Clarification by Membrane Filtration", PIRA Fourth International Wastepaper Technology Conference, 13-15 June 1995, Vol. 1, (1995).

14. **Upton, B.H., Krishnagopalan, G.A., Abubakr, S.**, "Deinking Flexographic Newsprint: Ultrafiltration Technology as a Method for Wash Filtrate Clarification", 1994 TAPPI Recycling Symposium Proceedings, May 15-18, Boston, MA, p.17, (1994).

15. **Upton, B.H., Krishnagopalan, G.A., Abubakr, S.**, "Deinking of Flexographic Newsprint: Use of Ultrafiltration to Close the Water Loop", 1995 TAPPI International Environmental Conference, May 7-10, Atlanta, GA, p.869, (1995).

16. **Wheeler, B.**, "ECHIP Version 6.0 for Windows® Reference Manual", ECHIP Inc., Hockessin, DE, p.10, 1993.

17. **Scheffe', H.**, "The Analysis of Variance", John Wiley & Sons, NY, p.223, 1959.

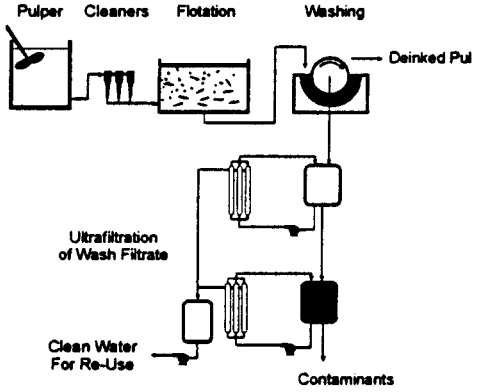

Fig. 1 Proposed flow scheme for ultrafiltration of wash filtrate.

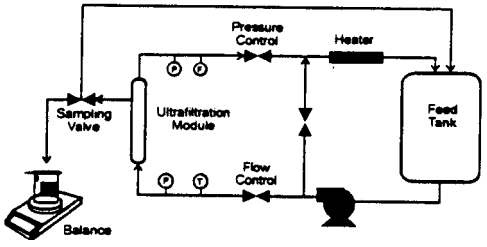

Fig. 2 Experimental Apparatus.

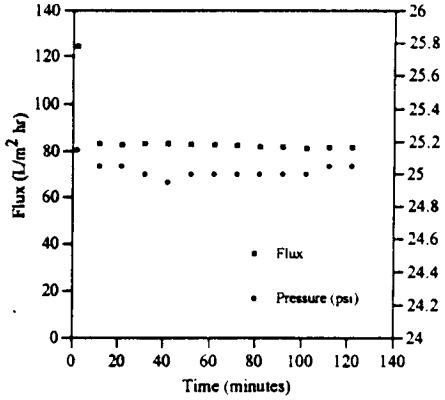

Fig. 3 Permeation rate vs. time, 50°C, 50,000 MWCO membrane, .5% surfactant, .11% ink.

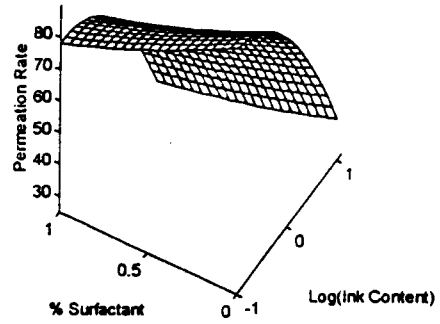

Fig. 4 Permeation rates using 10,000 MWCO membrane at 50°C.

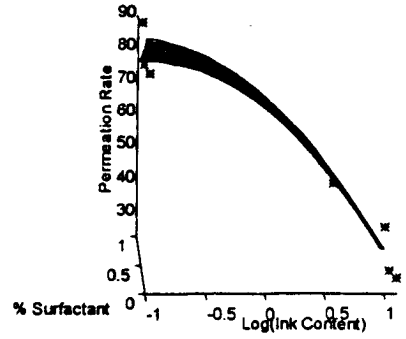

Fig. 5 Permeation rates using 10,000 MWCO membrane at 50°C.

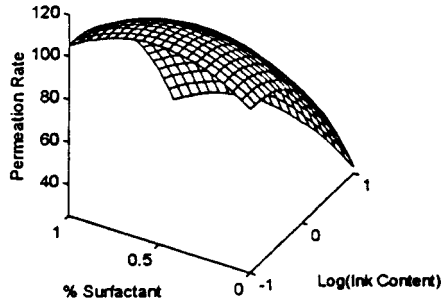

Fig. 6 Permeation rates using 500,000 MWCO membrane at 30°C.

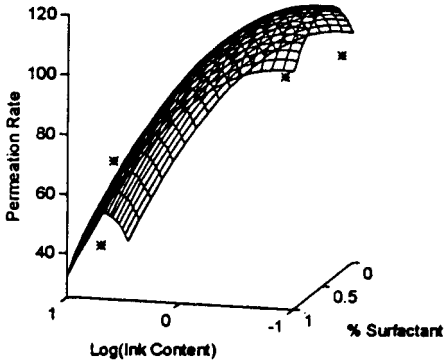

Fig. 7 Permeation rates using 500,000 MWCO membrane at 50°C.

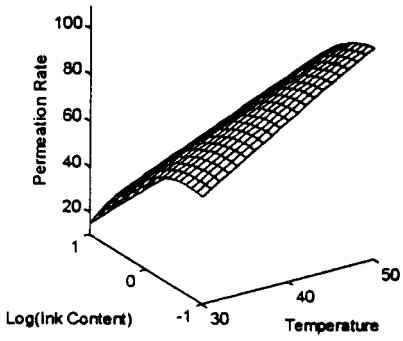

Fig. 8 Permeation rates using 10,000 MWCO membrane with no added surfactant.

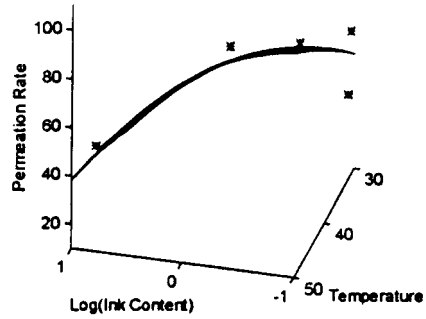

Fig. 9 Permeation rates using 10,000 MWCO membrane with no added surfactant.

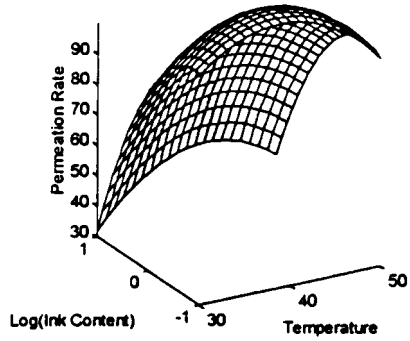

Fig. 10 Permeation rates using 500,000 MWCO membrane with 1% added surfactant.

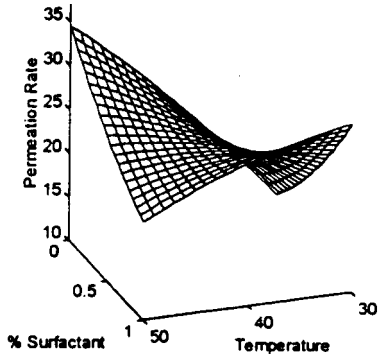

Fig. 11 Permeation rates using 10,000 MWCO membrane, 12% ink.

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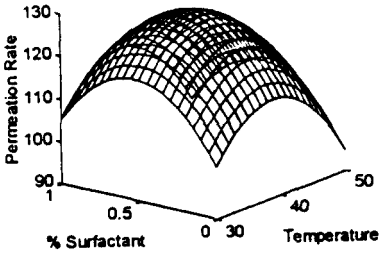

Fig. 12 Permeation rates using 500,000 MWCO membrane, .12% ink.

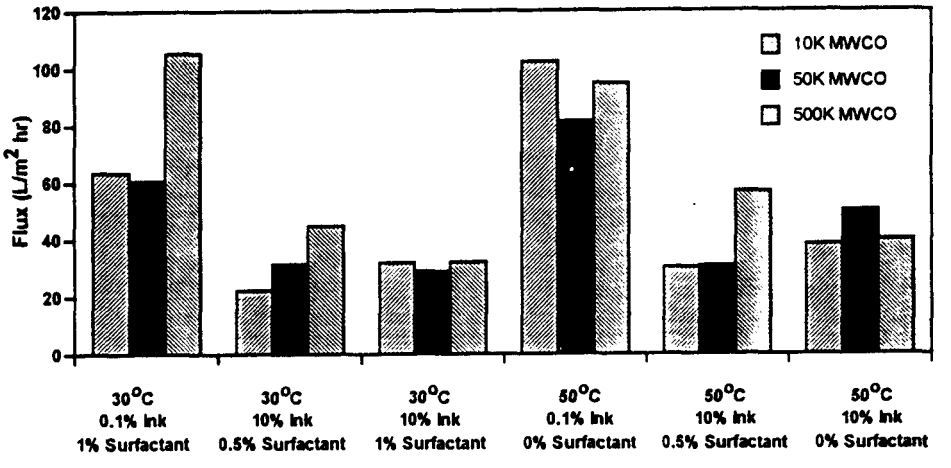

Fig. 13 Comparison of three membrane types.

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