Supercritical Carbon Dioxide Dewaxing of Old Corrugated Containers

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ABSTRACT: Wax-coated old corrugated containers (OCC) are not part of the paper recycling stream because a process to remove the wax coating is not presently available. Residual waxes influence fiber–fiber bonding, reducing the paper properties of recycled OCC as well as the paper machine operating efficiency. A procedure to dewax OCC is a major objective of the paper industry. Here we describe a novel process to quantitatively dewax OCC by using supercritical carbon dioxide to remove the wax. The results obtained for the extraction of both saturated and curtain-coated waxed containers are reported and compared with Soxhlet extraction with hexane. Quantitative removal of the waxes was obtained under a variety of operating conditions. Gas chromatographic analysis of the extracted paraffin wax shows that supercritical fluid extraction does not chemically alter the paraffin wax, indicating the recovered wax may be recycled. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1107–1114, 2001

Key words: supercritical fluid extraction; supercritical carbon dioxide; corrugated containers; wax removal; fiber recycling

INTRODUCTION

Corrugated containers are a primary packaging material that historically have held an advantage over other forms of packaging because of their recyclability.[1] However, wax-coated, old corrugated containers (OCC) are presently not part of the recycling stream because of the difficulties associated with removing the wax material from the board and the negative effects that wax contaminants have on the paper-making qualities of recycled OCC fiber and paper-making machinery.[2–4] Today, it is estimated that there are ~1 million tons of wax-coated corrugated containers produced each year in the United States.[1] Because these products are kept out of the recycling stream, they must be disposed of in landfills or incinerators.

Increasingly, the disposal of OCC is becoming less acceptable because of the environmental concerns these containers present. In addition to the environmental strain placed on already overcrowded landfills, waste haulers are further burdened by the high cost of disposal.[5] To overcome the current problems associated with the disposal and recycling of wax-coated OCC, there is a definite need for an alternative, more environmentally friendly method of recycling wax-coated

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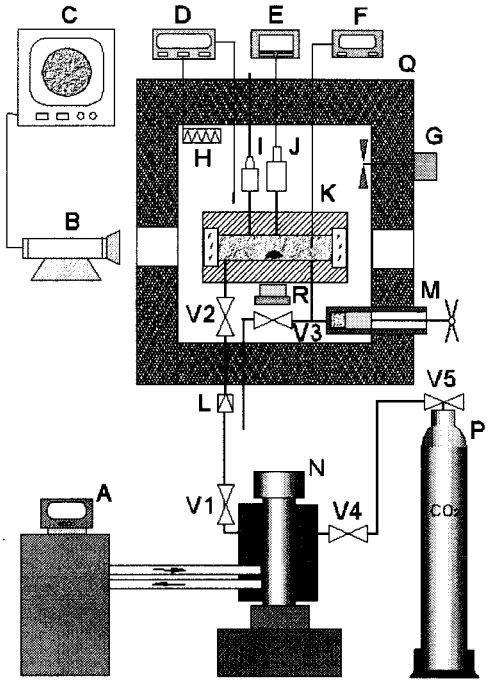

Figure 1 Experimental setup for solubility measurements: (A) thermostated bath; (B) video camera; (C) TV monitor; (D) temperature controller; (E) pressure display; (F) temperature display; (G) fan; (H) heater; (I) pressure relief valve; (J) pressure transducer; (K) view cell; (L) check valve; (M) pressure generator; (N) syringe pump; (P) CO_2 cylinder; (Q) air bath; ® stirrer; and (V1–V5) stop valves.

OCC. Here, the use of a novel process to quantitatively dewax OCC, namely, supercritical fluid extraction (SFE) with carbon dioxide ($SC–CO_2$) is reported.

In recent years there has been great interest in the use of supercritical fluids (SCFs) as solvents for chemical reactions and extraction processes. Important solvent properties of SCFs, such as viscosity, dielectric strength, and solubility parameter, can be controlled and systematically varied by manipulation of temperature and pressure.[6, 7] Conceivably these tunable properties of SCFs could be utilized to control the chemical behavior of a reaction (e.g., kinetics, selectivity) in a manner difficult to achieve with conventional solvents. $SC–CO_2$ is especially attractive because it is naturally occurring, readily available, and has an easily accessible critical point with a critical temperature (T_c) of 31.1 °C and a critical pressure (P_c) of 1070 psi. With its tunable density and low viscosity, $SC–CO_2$ has been shown to be an excellent solvent for chemical reactions, polymerizations, and extractions.

$SC–CO_2$ has already found wide application as an important industrial solvent for the extraction of lipophilic compounds and has replaced organic solvents for a variety of applications. For example, $SC–CO_2$ is currently used in processes such as the extraction of caffeine from coffee, fat from cocoa, and a variety of substances from hops and spices.[8] Increasingly, $SC–CO_2$ is finding application as an environmentally benign solvent for removing contaminants from a variety of materials, such as soil and wool.[9, 10] Recently, several reports have appeared in the literature describing the use of $SC–CO_2$ in the removal of paraffin waxes from injection-molded ceramics and military explosives.[11–14] In comparison with extractions with organic solvents, $SC–CO_2$ extraction has the principal advantages of being faster, more economical, and most importantly, environmentally benign.

The majority of wax coatings typically employed in the corrugated container industry are composed of paraffin wax. Paraffin wax is predominantly composed of straight-chain, *n*-alkanes with carbon backbone lengths ranging from C_{18} to C_{50} and averaging $C_{20}–C_{30}$. Several studies on the solubilities of various alkanes in $SC–CO_2$ have been reported.[15–18] The solubility behavior exhibited by the paraffin waxes should resemble the solubility behavior observed for the majority of the components (i.e., those with carbon backbones of C_{28} and lower in which *n*-alkanes with carbon numbers below C_{18} are completely miscible in $SC–CO_2$). Although the solubility of octacosane, C_{28}, in $SC–CO_2$ is marginal (0.09–0.89%, w/w, at lower temperatures (35–52 °C)), its solubility increases dramatically to 9.81% (w/w) at 90 °C.[19]

When used as a coating for corrugated containers, paraffin waxes generally contain modifiers that are used to achieve a variety of properties, such as increased durability, adhesion, scuff-resistance, plasticity, resistance to temperature extremes, and resistance to water. The addition of modifiers in general results in harder products with higher melting points. Modifiers also affect the bonding interactions between the paraffin wax and the OCC fiber. Saturating or cascading waxes are the most commonly employed in the corrugated container industry. A typical recipe for saturating wax consists of 95–99% paraffin wax and 1–5% modifier, usually a polymer or synthetic wax (e.g., a graft polymer of polyethylene and maleic anhydride with a low amount of functionality).[20] Curtain-coating waxes, in contrast to saturating waxes, are typically made

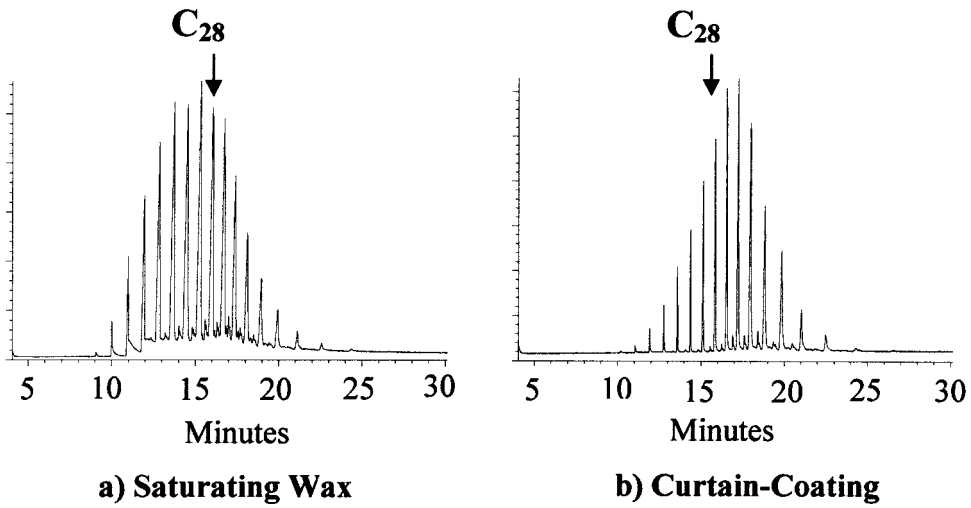

Figure 2 GC traces showing the distribution of *n*-alkanes in a saturated wax and a curtain-coating wax. C_{28} is octacosane.

from a higher melting basewax containing a greater distribution of higher molecular weight alkanes. They also contain more modifiers. As a result, the curtain-coating waxes are harder and have higher melting temperatures than saturating waxes.

MATERIALS AND METHODS

Materials

Curtain-coated and saturated waxed corrugated containers were obtained from Willamette Industries Incorporated, as were bulk samples of curtain-coating wax and saturating wax. The bulk wax samples and wax-board containers were preconsumer products and were used as received. "Bone-dry" carbon dioxide with a diptube was obtained from National Specialty Gases and chilled to 5 °C before pumping. Hexane (95% HPLC grade) and octacosane (99%) were obtained from Aldrich and used as received.

Solubility Measurements

The experimental setup used for investigating the solubilities of paraffin-based wax coatings in SC–CO_2 is shown in Figure 1. The high-pressure stainless steel view cell was loaded with a known amount of wax sample and filled with a known volume of CO_2. The air bath was heated to the desired temperature, and the entire system was allowed to attain thermal equilibrium. The high-pressure generator was used to pressurize the cell until the wax was dissolved. The phase equilibrium of the wax–CO_2 system was measured by decreasing the pressure in the cell until the wax precipitated from solution. The point of wax insolubility was determined by visual observation and the pressure and temperature were recorded.

Supercritical Fluid Extractions

Laboratory-scale supercritical fluid extractions were performed on a modified Suprex PrepMaster System using pure CO_2 as the solvent. OCC sam-

Table I Conditions for the Observation of Precipitation in the Curtain-Coating Wax SC–CO_2 System

	Observation of Precipitation						
Condition	1	2	3	4	5	6	7
Temperature (°C)	93.2	92.1	96.0	95.8	94.7	94.6	96.0
Pressure (psi)	4967	4214	3650	3478	3050	2649	1885

Table II Conditions and Results of Extractions with SC–CO_2

	$SC–CO_2$ Extraction			
	Curtain-Coating Wax		Saturating Wax	
Parameter	1st Trial	2nd Trial	1st Trial	2nd Trial
Weight of sample (g)	0.5247	0.5714	0.5228	0.5360
Temperature (°C)	100	100	100	100
Pressure (psi)	4350	4350	4350	4350
CO_2 flow (mL/min)	3.0	3.0	3.0	3.0
Time (min)	45	45	30	30
Weight after extraction (g)	0.4577	0.4964	0.3882	0.3936
Weight loss (%)	12.8	13.1	25.8	26.6

ples were cut into strips ~1 cm wide and 2.5 cm long and placed lengthwise into the extraction vessel. The extractions were semicontinuous in nature. Throughout the extraction process, CO_2 was vented through a heated (90 °C) restrictor valve into a collection chamber. To prevent clogging of the restrictor valve the extractions were performed in 15-min intervals. Immediately following each interval, the restrictor valve and collection chamber were rinsed several times with hexane. Immediately following the final extraction, the system was flushed with a mixture of SC–CO_2 and hexane, and the collection chamber was rinsed with hexane. The OCC from each extraction was immediately weighed without drying in an oven. The hexane rinses were collected and analyzed by gas chromatography (GC) for composition and distribution of extracted wax products.

Soxhlet Extractions

Soxhlet extractions of OCC were performed using cellulose thimbles with hexane as the solvent. OCC samples were cut into strips ~1 cm wide and ~10 cm long, weighed, and placed length wise into the thimbles. For each extraction, 300 mL of hexane was used and the extractions were allowed to proceed for 48 h. After the extractions were complete, the OCC and thimbles were removed from the Soxhlet apparatus and dried in a vacuum oven at 50 °C for 24 h before weighing. The filtrate was analyzed by GC to determine the composition and distribution of extracted wax components.

Analysis of Wax Samples

GC analyses of wax samples were performed with a Hewlett Packard 6890 gas chromatograph (splitless injection) with a flame ionization detector, using helium as the carrier gas. Injector and detector temperatures were 240 and 280 °C, respectively. Separations were achieved on a J&W DB-5 fused silica capillary column (30 m × 0.32 mm ×0.25 mm). The oven temperature was initially set at 120 °C and ramped at 10 °C/min to a

Table III Conditions and Results of the Soxhlet Extractions with Hexane

	Soxhlet Extraction (Hexane)			
	Curtain-Coating Wax		Saturated Wax	
Parameter	1st Trial	2nd Trial	1st Trial	2nd Trial
Weight of sample (g)	9.564	8.992	20.466	18.067
Temperature (°C)	RT	RT	RT	RT
Time (hours)	48	48	48	48
Weight after extraction (g)	8.302	7.917	15.066	13.407
Weight loss (%)	13.2	12.0	26.4	25.8

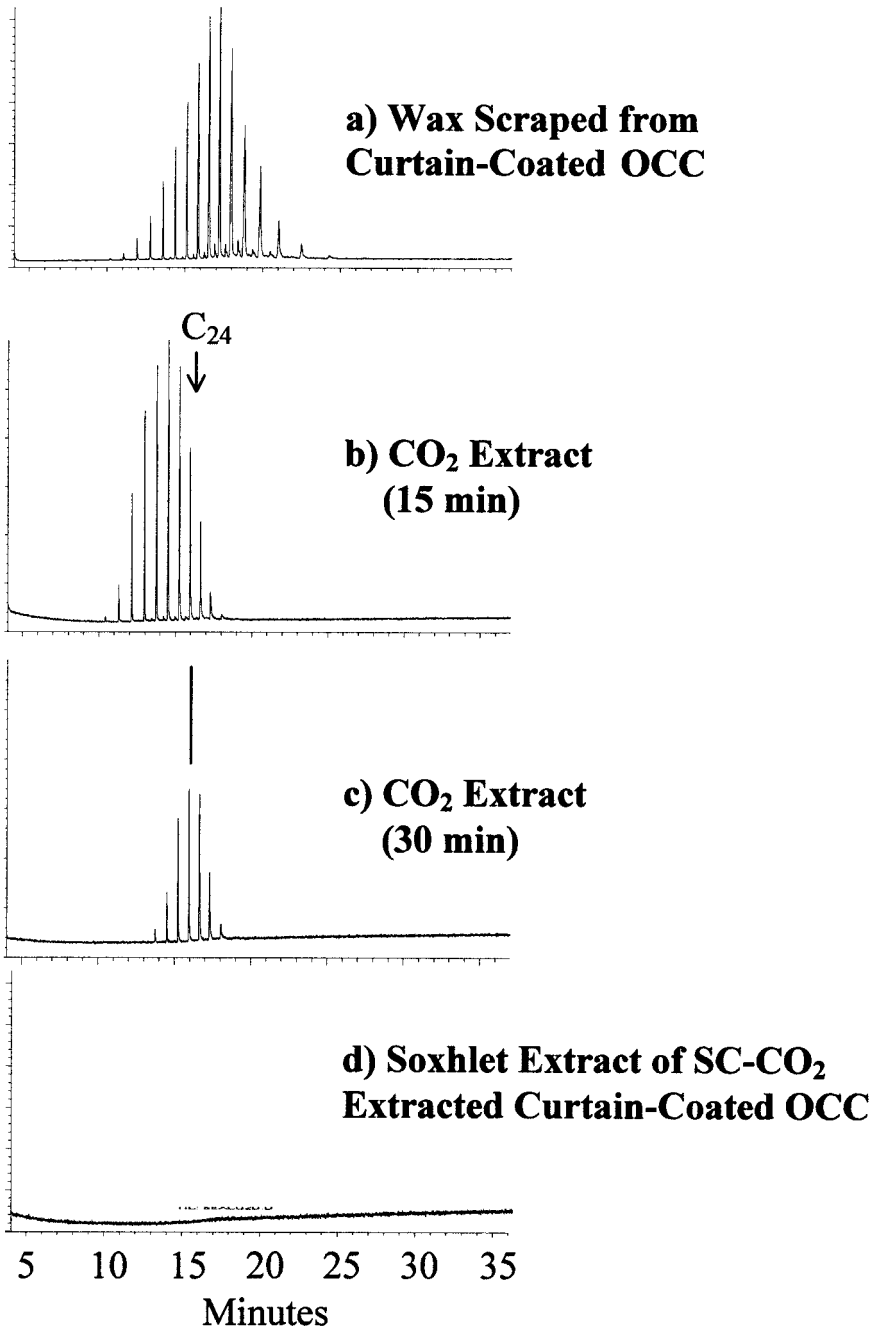

Figure 3 GC traces of (a) curtain-coating wax scraped from the surface of curtain-coated OCC; (b) SC–CO_2 extracts obtained at 15-min intervals during extraction of curtain-coated CC with SC–CO_2; and (c) Soxhlet extracts of the previously extracted (for 45 min with SC–CO_2) curtain-coated OCC.

final temperature of 280 °C. The final temperature was maintained for 45 min.

RESULTS AND DISCUSSION

The GC traces obtained on bulk samples of saturating and curtain-coating waxes used to coat the board samples are shown in Figure 2. Octacosane (C_{28}) was labeled to point out the differences in composition of the two samples.

Solubility Studies

For a solution of a pure substance in CO_2 at a constant composition and temperature, there ex-

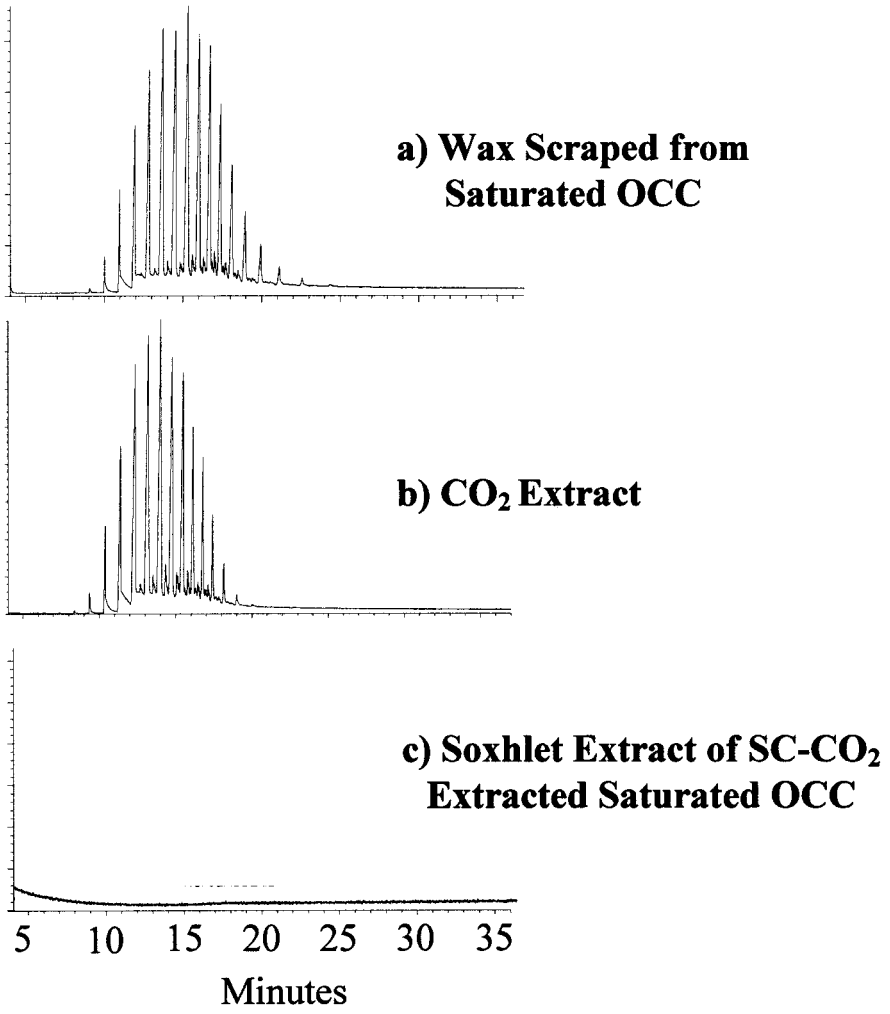

Figure 4 GC traces of (a) saturating wax scraped from the surface of saturated OCC; (b) SC–CO_2 extracts obtained at 15-min intervals during extraction of saturated OCC with SC–CO_2; and (c) Soxhlet extracts of the previously extracted (30 min with SC–CO_2) saturated OCC.

ists a very narrow pressure boundary that defines the point of solubility. At any pressure below this pressure boundary, the mixture is in a two-phase heterogeneous state, and, at any point above this pressure boundary, the solution is in a single-phase homogeneous state. As the pressure is decreased (isothermally) and the pressure boundary is reached, the substance precipitates out of solution almost instantly, giving the equilibrium pressure. However, in materials with a high degree of polydispersity, such as the paraffin-based waxes described herein, thermodynamically meaningful solubility measurements are not possible because at a given temperature and pressure, the lower molecular weight components will have greater solubility than will the higher molecular weight components,[15] resulting in the establishment of a new phase equilibrium. Therefore, the information obtained from the pressure–temperature study was used as guide to determine conditions suitable for the initial extraction experiments.

The behavior of the curtain-coating wax in SC–CO_2 was tested at temperatures near 60 and 100 °C. Solubility measurements were attempted on 0.0862 g (0.57%, w/w) of curtain-coating wax. At 60 °C and 6500 psi, there was no observable dissolution of the wax. The temperature was then raised to 98.6 °C in an attempt to dissolve the wax. These conditions were allowed to equilibrate overnight. Even at this high temperature and pressure, which are the limits of the apparatus, not all of the wax material went into solution as

evidenced by the presence of colorless droplets on the front and rear windows of the view cell and stir bar. The amount of undissolved material was indeterminable, but was sufficient to keep the stir bar from spinning. Despite this stir bar problem, observable changes in the system were noted as the pressure was lowered with a manual pressure generator. As the pressure was lowered from 6492 to ~5000 psi, the clear solution immediately turned dark. As the system was allowed to equilibrate, the solution became clear again and the amount of colorless droplets appeared to increase. As the pressure was then further lowered, six more precipitation events were observed. Shown in Table I are the conditions at which the seven observations were made for the curtain-coated sample,

Extractions with Supercritical CO_2

To determine the efficacy of SC–CO_2 as a suitable solvent for the removal of the various wax materials from OCC, representative samples of both curtain-coated and saturated wax board samples were extracted and analyzed for residual wax. The extractions were performed in duplicate at 100 °C and 4350 psi. The conditions employed for the SC–CO_2 extractions of the wax board samples and the resulting decreases in weight for each are shown in Table I. Extraction with SC–CO_2 under these conditions yielded an average decrease in weight of 13% for the curtain-coating wax samples and 26% for the saturating wax samples.

Soxhlet Extractions

Samples of both curtain-coated and saturated wax board were Soxhlet extracted in duplicate using hexane as the solvent. The conditions employed for the Soxhlet extractions and the resulting decreases in weight are given in Table III. The average decrease in weight for the curtain-coated samples was 12.6%, whereas the average decrease in weight for the saturated samples was 26.1%.

The results obtained for the SC–CO_2 extractions of the wax board containers correlate with the results obtained for the Soxhlet extractions. To determine whether the SC–CO_2 extractions completely removed the paraffin wax from the containerboard, the SC–CO_2 extracted samples were Soxhlet extracted for 24 h and analyzed by GC/mass spectrometry (MS).

The GC traces of the paraffin-based waxes scraped from the surfaces of curtain-coated and saturated corrugated containers are shown in Figures 3a and 4a, respectively. Also shown are the GC traces of the extracts obtained from the SC–CO_2 extractions (Figures 3b and c, and Figure 4b) and the subsequent Soxhlet extracts of the SC–CO_2 extracted boards (Figure 3d and Figure 4c). The results indicate that SC–CO_2 is effective at removing paraffin waxes from both types of wax-coated containerboard (Figures 3b and c and Figure 4b). GC analyses of the hexane extracts demonstrate that there is no residual wax on the SC–CO_2 extracted OCC (Figures 3d and 4c). The extraction of the saturated wax containers was achieved in 30 min compared with 45 min for the curtain-coated sample. This observed time differential might be due to higher levels of modifiers in the curtain-coated waxes. The results in Figure 3 further indicate that the waxes can be recovered in a variety of molecular weight ranges depending on the length of time of SFE using CO_2. Finally, the CO_2 extracts and the original wax GC traces are similar, suggesting that the CO_2 extraction process does not sufficiently chemically alter the wax. This result indicates the extracted wax may be recycled.

CONCLUSIONS

SC–CO_2 is a facile and effective process to dewax wax-coated corrugated containers. Quantitative removal of paraffin-based waxes were obtained at pressures of 4350 psi and a temperature of 100 °C. The SC–CO_2 extraction data are supported by the results of Soxhlet extractions with hexane. In addition to quantitative removal, the chemical nature and overall composition of the paraffin wax is unaffected by SC–CO_2 extraction, suggesting the recovered paraffin wax may be recycled.

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REFERENCES

1. Locke, R. E.; Kerr, J. C.; Vitori, C. M. TAPPI Proceedings 1998; 1998 Pulping Conference; pp. 313–319.
2. Drehmmer, B.; Back, E. L. Paper Technol 1995, 36–39.

3. Drehmmer, B.; Back, E. L. Prog Paper Recycling 1995, 4, 49–58.
4. McEwen, J. G. E. Prog Paper Recycling 1992, 11–20.
5. Stechmeyer, F., personal communication, 1999.
6. Phelps, C. L.; Smart, N. G.; Wai, C. M. J Chem Ed 1996, 73, 1163-1168.
7. Charpentier, B. A.; Sevenants, M. R. Supercritical Fluid Extraction and Chromatography; Comstock, M. J., Ed.; ACS: Denver, 1988.
8. Taylor, L. T. Supercritical Fluid Extraction; John Wiley and Sons: New York, 1996.
9. Montero, G. A.; Giorgio, T. D.; Schnell, K. B., Jr. ACS Symposium Series 1995, 608, 281–297.
10. Jones, F. W. J Agric Food Chem 1997, 45, 2569–2572.
11. Chartier, T.; Ferrato, M.; Baumard, J. F. J Am Ceram Soc 1995, 78, 1787–1792.
12. Chartier, T.; Ferrato, M.; Baumard, J. F. J Eur Ceram Soc 1995, 15, 899–903.
13. Chartier, T.; Delhomme, E.; Baumard, J. F. Ind Eng Chem Res 1999, 38, 1904–1910.
14. Ashraf-Khorassani, M.; Taylor, L. T. J Chem Eng Data 1999, 44, 1254–1258.
15. Schmitt, W. J.; Reid, R. C. Chem Eng Comm 1988, 64, 155–176.
16. Spee, M.; Schneider, G. M. Fluid Phase Equilib 1991, 65, 263–274.
17. Konrad, R.; Swaid, I.; Schneider, G. M. Fluid Phase Equilib 1983, 10, 307–314.
18. McHugh, M. A.; Seckner, A. J.; Yogan, T. J Ind Eng Chem Fundam 1984, 23, 493–499.
19. Bartle, K. D.; Clifford, A. A.; Jafar, S. A.; Shilestone, G. F. J Phys Chem Ref Data 1991, 20, 713–756.
20. Eastman Chemical Company, Kingsport, TN, Epolene Waxer Bulletin, 1996; pp.1–8.