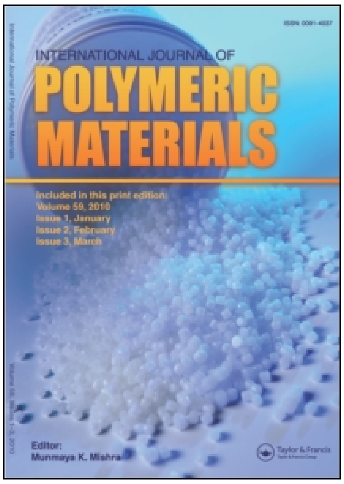

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# The Effect of Pressure and Temperature on Supercritical $CO_2$ Dyeing of PET-Dyeing with Mixtures of Dyes

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# The Effect of Pressure and Temperature on Supercritical $CO_2$ Dyeing of PET-Dyeing with Mixtures of Dyes

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Dyeing is supercritical $CO_2$ is one of the most advanced dyeing technologies. The dyeing medium is not water but carbon dioxide in the supercritical state (temperatures above 31°C and pressures above 74 bar).

The effect of pressure and temperature on dyeing of PET in supercritical $CO_2$ with only one dye and with mixtures of two or three dyes has been investigated.

The variations of pressure (250 in 300 bar) and temperature (70 in 130°C) cause differences in colour, especially when mixtures of dyes are used. The dyed samples were evaluated using colorimetry and the extraction of dyes from the fabric.

The amount of all dyes on the fabric rises with the rising temperature due to the accelerated motion of molecular chains and the formation of the free volume in the fibre, so important for the diffusion of dyes. The change of pressure does not alter the amount of fixed dyes significantly, but the ratio between the dyes is changed when dyeing with mixtures of dyes.

*Keywords:* Supercritical fluid dyeing; carbon dioxide; disperse dyes; dye mixtures; poliester PET

## 1. INTRODUCTION

All materials above the critical temperature and the critical pressure are supercritical fluids. Only one phase exists in the supercritical

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region, which is neither a liquid nor a gas, but it has the properties of both. The density and the dissolvability of supercritical fluids are similar to liquids, but the viscosity and the diffusion properties are similar to gases. By expansion or cooling under the critical temperature their solvent ability is lost and consequently the pulverised or liquefied solute falls out. $CO_2$ is the most widely used supercritical fluid because of its non-toxicity and low critical temperature and pressure.

Depending on the temperature and the pressure $CO_2$ can be gaseous, solid, liquid or supercritical, as shown in Figure 1.

At the triple point $T_{tr}$ (5,2 bar, – 56,5°C) the three phases, *i.e.*, solid (s), gas (g) and liquid (l), are in equilibrium. Here sublimation curve (s – g) ends and the melting (s – l) and the boiling (l – g) curves start. The melting curve rises steeply with pressure, and the boiling curve ends at the critical point CP (74 bar, 31°C). Above the critical pressure (74 bar) and temperature (31°C) $CO_2$ is a supercritical fluid. The density of liquid and gas is equal.

Supercritical $CO_2$ has been used for quite a long timer. Well-known are extraction processes, *i.e.*, extraction of caffeine, hop and other natural substances, generally used in the pharmaceutical, cosmetics and food industry. Recently, the supercritical fluids have been utilised as solvents for non-extractive applications in high pressure micronisation, in chromatography and as chemical and biochemical reaction

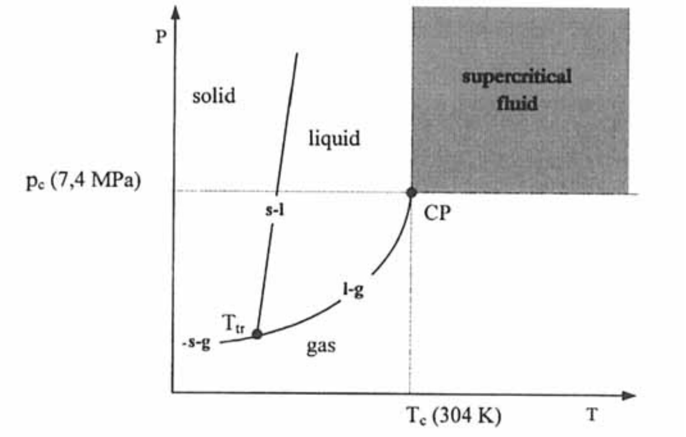

FIGURE 1 Phase diagram of $CO_2$.

media [1]. Supercritical $CO_2$ is used also as a medium for textile finishing. Dyeing in supercritical $CO_2$ has become very interesting.

The dyeing medium is not water, but supercritical $CO_2$. The key property of supercritical $CO_2$, that makes the dyeing possible is its ability to dissolve hydrophobic substances including disperse dyes. The supercritical fluid has two tasks in the dyeing process: it heats the substrate and transports the dyes [2]. The process can be controlled by temperature and by pressure.

The dyeing of PET (the most widely used textile fibre) in supercritical $CO_2$ is very interesting. Most of the research work on the use of supercritical $CO_2$ in textile applications was made by the research group of the German institute DTNW under the leadership of dr. E. Schollmeyer [2–7, 10–11]. According to literature, the dyeing of PET in supercritical $CO_2$ should be performed at a pressure above 180 bar and a temperature above 70°C [2]. The published results deal only with the behaviour of one dye in supercritical $CO_2$, but dyeing with mixtures of dyes, which is the most important in industrial practice, has remained unknown consequently, we decided to study the effect of the dyeing temperature and pressure on dyeing of PES using one dye or mixtures of two or three dyes.

The changes in the amount of a dye on the fabric has been followed by the extraction of the dyed fabric with hot chlorobenzene and determined with VIS spectrometry. The investigation of dyeing in supercritical $CO_2$ with mixtures of dyes is a new original contribution to science.

## 2. EXPERIMENTAL

### 2.1. Materials

Washed 100% PES fabric was used in the dyeing experiments.

The dyeings were performed with three disperse dyes, developed by CIBA for supercritical fluid dyeing. The chemical constitution is a commercial secret, only molecular masses are given with the accuracy of ± 5%. The code names of dyes are:

1. $CO_2$ PES Gelb SM2P, M = 360 g/mol
2. $CO_2$ PES Rot SM2P, M = 430 g/mol
3. $CO_2$ PES Blau SM1P, M = 400 g/mol

In the next they will be referred to as yellow, red and blue.

$CO_2$ was 99,99% (by volume) pure and supplied by LINDE plin, Celje, Slovenia.

### 2.2. Dyeing Conditions

Individual dyes (yellow, red and blue) were used as well as a mixture of the red and blue dye (mass ratio 1 : 1) and a mixture of the yellow, red and blue dye (mass ratio 1 : 1 : 1). The dyeings were performed with 3% of individual dyes or mixtures of dyes per weight of fabric. The dyeing conditions were as follows:

1. 70°C, 250 bar
2. 70°C, 300 bar
3. 130°C, 250 bar
4. 130°C, 300 bar

The dyeing time was 20 min.

### 2.3. Dyeing Apparatus

All samples were dyed in static high pressure apparatus for dyeing in supercritical $CO_2$, as shown in Figure 2. The dyebath was circulating only inside the autoclave due to the rotation of the magnetic stirrer.

Approximately 0,5 g of fabric, 3% of dye or mixture of dyes and the magnetic stirrer were put inside the 0,121 autoclave (5). The $CO_2$ from the supply tank (1) was cooled to the liquid state and then pumped into the autoclave by means of a high pressure pump (4). When the pressure of 20 bar was reached, the system was briefly thermostated to attain the working temperature. Afterwards, in approx. 15 min, the pressure risen to the working pressure. The dyeing was accomplished in 20 min at isobaric and isothermic conditions. Later, the heating oil bath was removed and in approx. 5 min $CO_2$ was expanded. The dyed samples were rinsed with acetone to remove the unfixed dye.

## 3. RESULTS AND DISCUSSION

The effect of temperature and pressure on the amount of sorbed dyes determined by the extraction of dyed samples with not chlorobenzene

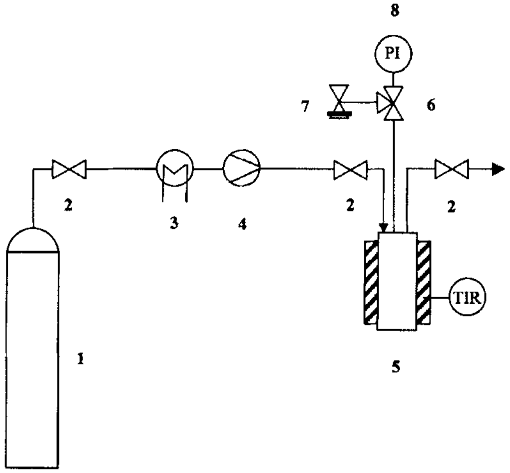

FIGURE 2 Apparatus for dyeing in supercritical $CO_2$; 1 – $CO_2$ tank, 2 – high pressure valves, 3 – heat exchanger, 4 – high pressure pump, 5 – autoclave with external heating, 6 – T piece, 7 – safety valve, 8-manometer.

is shown in Tables I – III. Table I shows the results for samples dyed with individual dues, Table II the results for dyeings with a mixture of the red and blue dye, and Table III the results for dyeings with a mixture of the yellow, red and blue dye.

The highest amount of fixed dyes is attained at 130°C and 300 bar. Under certain conditions the blue dye has the highest, the red dye a little lower and the yellow dye the lowest fixation rate. The pressure and the temperature positively influence the amount of fixed dyes; with the raising temperature and pressure the quantity of dyes on the fabric raises, too.

The dyeing temperature has the greatest influence on the amount of the sorbed dye. At 130°C a larger amount of dye is sorbed than

TABLE I The effect of the temperature ($T$) and pressure ($P$) on the amount of sorbed dyes ($X$) when dyeing with individual dyes

| | | X(mg/g) | | |
|---|---|---|---|---|
| T(°C) | P(bar) | Yellow | Red | Blue |
| 70 | 250 | 0,139 | 0,149 | 0,156 |
| 70 | 300 | 0,248 | 0,152 | 0,218 |
| 130 | 250 | 4,938 | 5,360 | 6,058 |
| 130 | 300 | 5,265 | 6,352 | 7,347 |

TABLE II The effect of the temperature ($T$) and pressure ($P$) on the amount of sorbed dyes ($X$) when dyeing with a mixture of the red and blue dye in the mass ratio 1 : 1

| | | *X(mg/g)* | | |
|---|---|---|---|---|
| *T(°C)* | *P(bar)* | *Red* | *Blue* | *Total* |
| 70 | 250 | 0.133 | 0,112 | 0,245 |
| 70 | 300 | 0,144 | 0,091 | 0,235 |
| 130 | 250 | 4,153 | 3,842 | 7,995 |
| 130 | 300 | 4,633 | 3,234 | 7,867 |

TABLE III The effect of the temperature ($T$) and pressure ($P$) on the amount of sorbed dyes ($X$) when dyeing with a mixture of yellow, red and blue dye in the mass ratio 1 : 1 : 1

| | | | *X(mg/g)* | | |
|---|---|---|---|---|---|
| *T(°C)* | *P(bar)* | *Yellow* | *Red* | *Blue* | *Total* |
| 70 | 250 | 0,071 | 0,048 | 0,035 | 0,154 |
| 70 | 300 | 0,062 | 0,057 | 0,014 | 0,133 |
| 130 | 250 | 3,497 | 1,829 | 1,603 | 6,929 |
| 130 | 300 | 2,665 | 2,391 | 1,471 | 6,527 |

at 70°C. The temperature of 70°C is obviously not high enough to cross the glass transition point needed for successful diffusion of dyes into the fibres. The greatest differences between dyeings at 70°C and 130°C occur by dyeing with the blue or red dye, because their molar masses are higher than the molar mass of the yellow dye. The formation of an adequate free volume is more important for dyes with a higher molar mass. Increased pressure at a constant temperature cause higher dye uptake. The higher the pressure is, the greater is the density of $CO_2$, and the more of the dye can be dissolved [1].

If the total amount of the red and blue dye in Table II is compared with results in Table I we can observe similar trends. In contrast to Table I, the results in Table II show an interesting phenomenon; the total amount of fixed dyes decreases with the increasing pressure at constant temperature, which could indicate a better migration of dyes at higher pressure. The phenomenon is still under investigation.

The most important element, when dyeing with a mixture of dyes, is the ratio of the amounts of dyes on the fabric. Every change causes a change in hue.

Dyeing with a mixture of two dyes at 130°C results in a much higher amount of red and blue dye on fabric in comparison with dyeing at 70°C, which is explained to the above mentioned reasons. The difference in dye uptake can be up to 30 times as high.

With the rise of pressure from 250 bar to 300 bar at constant temperature, 10% more of red and 20% less of blue dye is sorbed; therefore the total uptake is only slightly changed-more important is the change in hue. The blue dye has smaller molecules than the red dye, so by theory it migrates easier [12]. Because of its better migration properties the blue dye probably sets free the locations in fibres, which are occupied by the red dye.

The dyeing with the mixture of three days (Tab. III) gives higher total amounts of fixed dyes than dyeing with the mixture of two dyes, which indicates that dyes compete for accessible locations in fibres and exhibits the importance of the presence of the yellow dye, which has the smallest molar mass and the best migration abilities.

At 130°C the amounts of dyes are 40–50 times as high as at 70°C. Raising the pressure from 250 bar to 300 bar at a constant temperature eventuates the decrease in the amount of the yellow dye (at 70°C approx. 10%, and at 130°C approx. 20%), the increase of the amount of the red dye (at 70°C approx. 20% and at 130°C approx. 40%) and decrease of the amount of the blue dye (at 70°C approx. 50% and at 130°C approx. 10%).

When dyeing with mixtures of dyes at various temperature and pressures noticeable colour differences between dyed samples are observed (Tab. IV).

The results show that the effect of pressure on total colour differences is smaller at higher temperatures.

TABLE IV CIELAB colour differences of samples dyed with mixtures of dyes (at standardised light source D65)

| *Standard* | *Sample* | $\Delta L^*$ | $\Delta a^*$ | $\Delta b^*$ | $\Delta C^*$ | $\Delta H^*$ | $\Delta E^*$ |
|---|---|---|---|---|---|---|---|
| | | | | *Red + Blue* | | | |
| 70°C<br>250 bar | 70°C<br>300 bar | −2,9 | 2,3 | 0,4 | 2,2 | 0,6 | 3,7 |
| 130°C<br>250 bar | 130°C<br>300 bar | −0,2 | 1,5 | 1,8 | 1,0 | 2,1 | 2,4 |
| | | | *Red + Blue + Yellow* | | | | |
| 70°C<br>250 bar | 70°C<br>300 bar | −4,4 | 1,8 | −2,9 | −1,9 | −2,8 | 5,6 |
| 130°C<br>250 bar | 130°C<br>300 bar | −1,1 | 3,3 | −3,2 | −1,3 | −4,4 | 4,7 |

Samples dyed at 70°C and various pressures give greater colour differences than samples dyed at 130°C. The shifts on $a^*$ and $b^*$ axes result in differences in hue. A sample dyed with a mixture of two dyes at higher pressure is redder and less blue. A positive difference of position on the $a^*$ axis in the case of samples dyed with a mixture of three dyes at higher pressure means a redder colour.

## 4. CONCLUSION

Dyeing in supercritical $CO_2$ can be controlled with temperature and with pressure. Both of them affect the amounts of dyes fixed on fabric. Higher pressures and temperatures increase the amount of the fixed dye when the dyeing is performed with only one dye. The movement of macromolecules in PES fibres is faster at higher temperatures. It is important that the dyeing temperature is higher than the glass transition point of fibres to ensure the formation of sufficient free volume needed for the diffusion of dyes into the fibres.

The raise in pressure from 250 to 300 bar does not have the same influence on the amount of fixed dyes as the raise of temperature from 70 to 130°C. When the dyeing is performed with mixtures of dyes, the changes in the dyeing temperature and pressure result in colour differences, *i.e.*, in lightness as well as in hue.

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