

Thermal Behavior of Silver Behenate-based Dry Processable Image-forming Materials

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Abstract

Silver salts of straight chain alkyl carboxylic acids with 12-22 carbon atoms are the principal ingredients of dry processable thermographic and photothermographic image-forming materials. Thermography is based on the reduction of these silver salts by image-wise heating. Since heat plays a very important role in the silver behenate development process, the thermal behavior of silver behenate crystals has been studied by high temperature X-ray diffraction.

A method was developed to monitor the in-situ changes in X-ray diffraction patterns with temperature. The formation of new crystalline structures, crystal structure changes and phase transitions were identified. The amorphization of the silver behenate starts at 120°C and is irreversible. New crystalline structures were observed at higher temperatures, which could be associated with silver behenate in different crystalline and liquid crystalline states. Three distinct phases were identified. The phase transitions between these crystalline and liquid crystalline phases are reversible. Further heating results in the crystal melting. Formation of behenic acid and silver is first observable at 180°C, indicating decomposition of the silver behenate crystals.

Introduction

Silver salts of straight chain alkyl carboxylic acids with 12-22 carbon atoms are the principal ingredients of dry thermally processable image-forming materials (1). Thermography is based on the reduction of these silver salts by image-wise heating with an IR laser or thermal head, a linear array of heating elements. This results in decomposition of the silver salt and formation of metallic silver in the form of a visual image and the corresponding acid (2,3,4,5,6).

Silver behenate is suitable for dry processable systems, because it is both insensitive to visible light and has an acceptable thermal developability. Since heat plays a very important role in the silver behenate development process, the thermal behavior of silver behenate crystals has been studied by high temperature X-ray diffraction.

Experimental

Instrumentation

XRD-measurements were carried out with a powder diffractometer, Philips X'Pert system, equipped with a high temperature chamber with which it is possible to monitor the in-situ changes in XRD-diffraction patterns with temperature. This enables both crystalline structures to be identified at room temperature and crystal structure changes and phase transitions to be determined at high temperatures.

The XRD spectra were acquired with a $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$) X-ray source at 40keV and 50mA. A continuous scan $\theta/2\theta$ was used. The step-width, time per step and the diffraction angle range, depending on the type of experiment and details studied, are typically 0.030° , 0.9s and 1 to $70^\circ 2\theta$. The temperature was varied from room temperature up to 200°C , the relevant range for thermographic and photothermographic materials. The measurements can be performed with a stability of 1°C and can be reached within seconds.

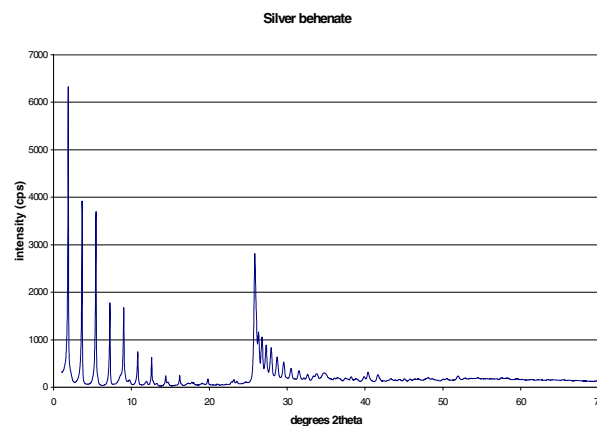


Figure 1. X-ray diffraction pattern of silver behenate at room temperature.

Sample Preparation

Silver behenate was measured directly in the XRD instrument using a backloading sample holder aimed at eliminating as far as possible any preferential orientation. A typical spectrum is visualized in figure 1. For this specific high resolution spectrum a small step-width and a long time per step, typically 0.02° and 60s, was used.

For the temperature experiments the silver behenate was loaded into a high temperature Pt holder. The temperature was monitored during the experiments.

Results

Silver formation

If pure silver behenate was heated for milliseconds no measurable amount of silver was formed. If longer heating was performed, silver is formed at temperatures at or above 180°C , the amount of silver formed increasing with increasing temperature as can be seen from figure 2, in which the silver formation is plotted as a function of temperature. The average crystallite size of these Ag clusters was between 4 and 10nm according to the Scherrer formula (7):

$$D = K\lambda / [\cos\theta(\beta - \beta_s)]$$

where D is the crystallite size (nm), K , a form factor (no dimensions), λ , the wavelength of the incident X-rays, β , the full width at half maximum of the diffraction peak (in rad), β_s , the full width at half maximum originating from the instrument and θ , the peak position (in rad).

Crystalline behenic acid could only be detected upon cooling to room temperature.

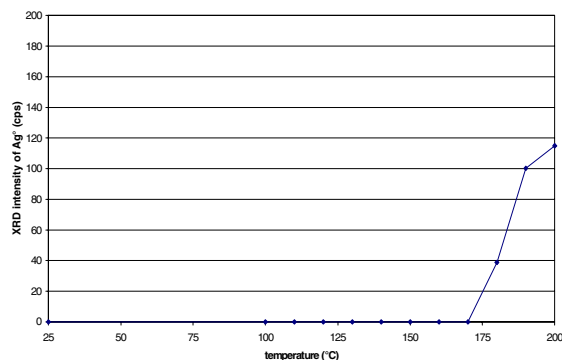


Figure 2. Ag^0 formation as a function of temperature

Phase transitions

Silver behenate is a crystalline powder at room temperature. It has been used as an XRD standard for the calibration at low angle diffraction (8,9). A method for determining the relative crystallinity of silver behenate has been previously reported (10).

From 120°C a considerable loss of crystallinity was observed. This phenomenon may be associated with the paraffin chains becoming less ordered. The silver behenate changed from a crystalline state into an amorphous state. At 130°C the amorphization was much stronger. This was an irreversible process. Upon cooling the silver behenate, after heating the sample up to 200°C , the crystalline phase was only reformed to a small extent (figure 3). Prolonged heating may even render recrystallization impossible (figure 4). The original crystal structure is never obtained again, the first amorphization is irreversible.

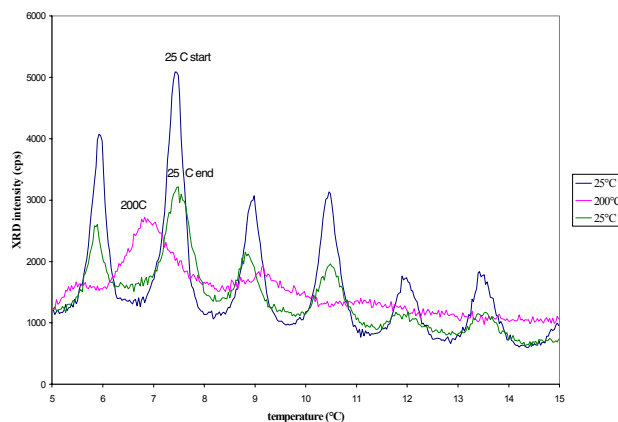


Figure 3. Recrystallization of silver behenate after temperature treatment for seconds

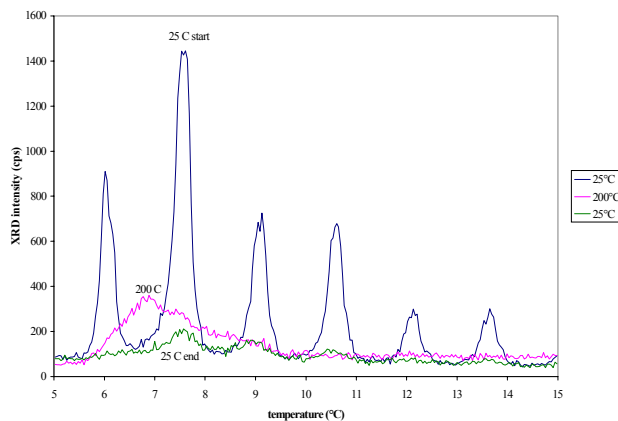


Figure 4. Recrystallization of silver behenate: irreversible process due to heating for minutes

At $138\text{--}142^\circ\text{C}$ other diffraction peaks were observed, which indicated a change in crystal structure and the first phase transition. This phase (phase 2) exhibited diffraction peaks at low 2θ -values, indicating that the paraffin chains had become partly intercalated in the previously ordered paraffin chain structure. At 145°C it was changed into a mesomorphic phase (phase 2bis) smectic A. This was confirmed by polarization microscopy (figure 5). The liquid crystal phase was clearly visible by touching the sample holder. The bright zones in figure 5 correspond with the

silver behenate chains parallel to the microscope axis. The dark zones correspond with chains perpendicular to the axis.

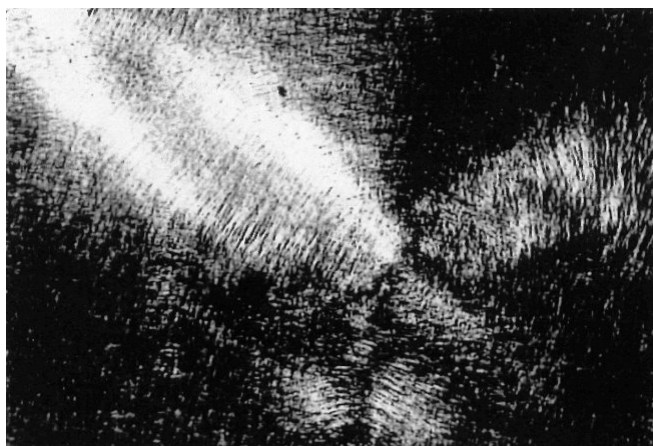


Figure 5. Image of silver behenate in liquid crystal phase using polarization microscopy.

From 156°C further changes were observed in the lattice spacing, indicating a second phase transition. The mesomorphous phase 3 was formed. Here the insertion of paraffin chain in the previously ordered structure was more pronounced. Both phase transitions between crystalline phases were reversible. Upon cooling, the transitions took place at the same temperatures and phase 3, as well as phase 2bis and 2 were formed (figure 6). The amount of mesomorphous phase formed during cooling was more pronounced, as is the case with most liquid crystalline material.

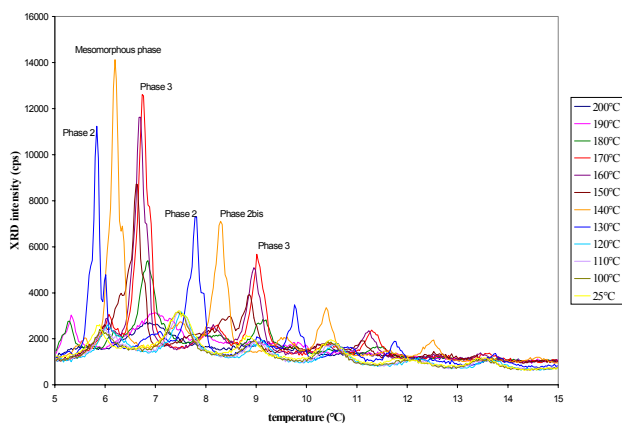


Figure 6. In-situ cooling profile: XRD diffraction patterns at different T

Further heating resulted in the crystal melting. Formation of silver and behenic acid was first observed above 180°C, indicating decomposition of the silver behenate crystals. Above 200°C fast decomposition was observed. In figure 7 an overview of the formation and decomposition of the different silver behenate phases is presented. The different diffraction peaks observed at different temperatures are summarized in table 1.

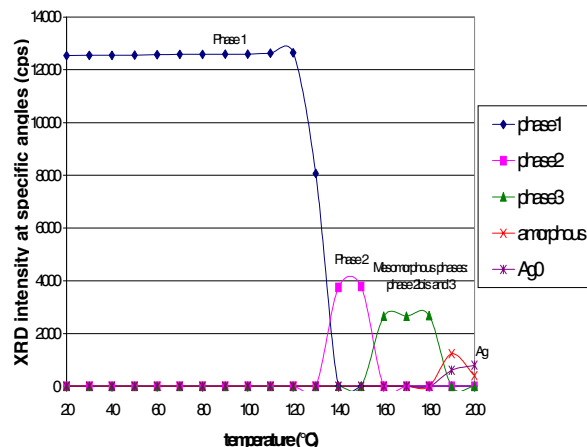


Figure7. XRD intensities calculated at specific angles representative for the crystalline, liquid crystalline or amorphous phase.

25°C	100°C	110°C	120°C	130°C	140°C
5.962	5.948	5.947	5.928	5.953	5.442
7.466	7.457	7.455	7.443	7.463	6.118
8.998	8.985	8.982	8.974	8.992	7.728
10.525	10.505	10.509	10.490	10.503	8.420
12.051	12.029	12.035	11.996	12.049	9.275
13.572	13.552	13.559	13.541	13.575	10.816
					12.483
150°C	160°C	170°C	180°C	190°C	200°C
5.692	6.160	6.190	6.244	6.783	/
6.322	6.805	6.845	6.925	9.016	
7.680	8.259	8.329	8.417	9.987	
8.531	9.234	9.186	9.243	10.852	
9.808	10.316	10.630	10.696		
10.642	11.242	11.504	11.559		

Table 1. Summary of the diffraction peaks in degrees 2θ of silver behenate observed at different temperatures.

Conclusion

Silver behenate forms a crystalline powder at room temperature. Above 120°C amorphization took place. During temperature treatment different crystalline and mesomorphous phases were formed. New crystalline structures were observed at higher temperatures, which could be associated with silver behenate in different crystalline and liquid crystalline states. Three distinct phases could be identified. The phase transitions between crystalline phases were reversible. Further heating resulted in the crystal melting.

References

1. B.B. Bokhonov, O.I. Lomovsky, V.M. Andreev and V.V. Boldyrev, *J. Solid State Chem.*, **58**, 170 (1985).
2. I. Geuens, I. Vanwelkenhuysen, Physical Characterization of Silver Behenate as a Tool for the Development of Thermographic and Photothermographic materials, *Proc. ICPS98*, 51pg (1998).
3. E.K. Fields and S. Meyerson, *J. Org. Chem.*, **41**, 916 (1976).
4. B. B. Bokhonov, L.P. Burleva, W. Frank, M.B. Mizen, D.R. Whitcomb and C. Zou, *J. Imag. Sci. and Techn.*, **40**, 417 (1996).
5. Y. E. Usanov and T.B. Kolesova, *J. Imag. Sci. and Techn.*, **40**, 104 (1996).
6. P.Z. Velinzon, S.I. Gaft, B.M. Serebryanyi, L.V. Krasnyi-Admoni and P.M. Zavlin, *Sci. Appl. Photo.*, **37**, 651 (1996).
7. Klug & Alexander, *X-Ray Diffraction Procedures*, Wiley, 1954.
8. T.N. Blanton, T.C. Huang, H. Toraya, C. Hubbard, S. Robie, D. Louër, H. Göbel, G. Will, R. Gilles, T. Raftery, *Powder Diffr.*, **10**, 91 (1995).
9. T.C. Huang, H. Toraya, T.N. Blanton, *J. Appl. Cryst.*, **26**, 180 (1993).
10. I. Geuens, I. Vanwelkenhuysen, *J. Imag. Sci.*, **43**, (1999).
11. Gerhard Meier, Erich Sackmann, J.G. Grabmaier, *Applications of Liquid Crystals*, Springer Verlag, Berlin-Heidelberg-New York, 1975.
12. M. Ikeda, *Photogr. Sci. Eng.*, **24**, 277 (1980).
13. K. Binnemans, B. Heinrich, D. Guillon, D.W. Bruce, *Liq. Cryst.*, **26**, 1717 (1999).
14. K. Binnemans, L. Jongen, C. Görller-Walrand, *Eur. J. Inorg. Chem.*, in press.