

A Study of Curative Interactions in the Presence of Cobalt(II) Stearate

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ABSTRACT: The curative interactions with the participation of dicyclohexylbenzothiazole-2-sulfenamide (DCBS), stearic acid (SA), ZnO, S, and Co(II) stearate (octadecanoate- CoC_{18}) as adhesive promoter have been investigated by means of DSC calorimetry, EPR, and IR spectroscopy in the absence of rubber. It has been found that in the presence of CoC_{18} , DCBS, and S, structural changes have been observed on the action of heat, which are connected with the formation of polysulfide complexes between Co^{2+} ions, DCBS fragments, and sulphur. In the presence of SA and ZnO in the five-component system, zinc(II) octadecanoate is formed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2936–2943, 2001

Key words: curative interaction; Co(II) stearate; DSC calorimetry; EPR spectroscopy; IR spectroscopy

INTRODUCTION

Although the chemistry of vulcanization of natural rubber with sulphur has been intensively studied, reports on the interaction between the vulcanizing ingredients are few. Kok¹ indicated that the reaction between the sulfenamide accelerator, zinc oxide, and stearic acid can be observed by thermal analysis. However, in agreement with Kruger and McGill,² it is possible that the formation of zinc stearate was mistakenly identified by Kok as a complex formation between these ingredients. Tsai and Boerio³ studied the interactions between a plasma polymerised primer and a mixture of squalene, zinc

oxide, carbon black, sulphur, stearic acid, cobalt naphthenate, and *N,N*-dicyclohexylbenzothiazole-2-sulfenamide (DCBS). They found that ZnO and cobalt naphthenate reacted with stearic acid to form zinc stearate and cobalt stearate, which then reacted with DCBS to form zinc and cobalt acceleration complexes. Chandra and co-workers^{4,5} have carried out systematic investigations of the influence of cobalt promoters on the adhesion energy and curing reactions, and they assumed that Co^{2+} ion forms a chelate complex with the accelerator and the accelerator fragments.

This work is a continuation of our previously reported studies^{6–8} on the mutual interactions of curatives with the participation of metal carboxylates as adhesion promoters. Possible interactions between cobalt(II) stearate (CoC_{18}) and *N,N*-dicyclohexylbenzothiazole-2-sulfenamide (DCBS), stearic acid (SA), zinc oxide (ZnO), and

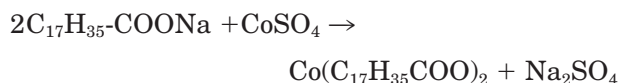
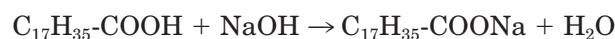
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sulphur (S) have been studied by differential scanning calorimetry (DSC), infrared, and EPR spectroscopy in the absence of rubber.

EXPERIMENTAL

All rubber chemicals were purchased from local supplier (MERCK s.r.o.), and used without further purification. Cobalt(II) octadecanoate was prepared in the reaction between a heated aqueous solution of sodium salt of the corresponding carboxylic acid with the heated aqueous solution of cobalt(II) sulphate:



The prepared sample was washed with ethanol and dried at approximately 100°C. For $\text{Co}(C_{17}H_{35}\text{COO})_2$, calculated: 9.41% Co; 69.08% C; 11.27% H; found: 9.30% Co; 68.78% C; 11.56% H. All mixtures prepared had been intensively ground.

The Perkin-Elmer Differential Scanning Calorimeter DSC-7 was used for the DSC studies (the null balance power compensating principle, a sample mass of 1.5–5 mg, pure nitrogen and scanning rate of 10°C min⁻¹). Calibration of the temperature and change of enthalpy axes were made with pure indium with the melting point of 156.6°C and $\Delta_f H = 28.47 \text{ J} \cdot \text{g}^{-1}$.

The infrared absorption spectra were measured in KBr tablets with the Philips PU 9800 FTIR spectrophotometer in the range of 4000–400 cm⁻¹.

The EPR spectra were recorded on a Bruker SRC-200 D spectrometer coupled to an Aspect 2000 and equipped with a variable temperature unit.^{9,10} Line positions were measured accurately using internal field markers generated by an NMR gaussmeter, while the microwave frequency was measured by a microwave frequency counter. A 100-kHz magnetic field modulation (peak-to-peak amplitude ~ 3 Gauss) was used.

RESULTS AND DISCUSSION

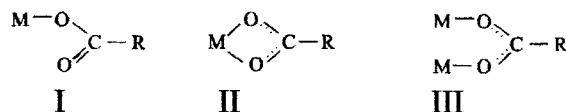
One of the basic criteria influencing the properties of car tyres is the adhesion of the rubber

compound to the steel cord. To achieve a high degree of rubber-to-metal adhesion, it is necessary to use an important group of substances known as adhesion promoters. For the “rubber–steel cord” system, adhesive agents based on the carboxylates of metals $M(\text{R-COO})_2$ have proven successful.¹¹ In the present work we were concerned with the study of the influence of cobalt(II) stearate on the curative interactions by means of DSC calorimetry, infrared, and EPR spectroscopy.

DSC and Spectral Studies of Individual Components

DSC studies of the phase changes occurring on heating long-chain carboxylates of various divalent metal ions have shown the importance of the metal ion in determining its behavior. Thus, lead(II) and cadmium(II) carboxylates form liquid crystalline mesophases, zinc(II) soaps melt directly from solid to isotropic liquid.¹² The similarity of the ionic radii of cobalt(II) (72 pm) and zinc(II) (74 pm) implies some similarity in the electrostatic interactions in the Co(II) and Zn(II) carboxylates. It is therefore not too surprising to observe that Co(II) stearate (CoC_{18}), like Zn(II) soaps, melts at ~ 104°C from solid to isotropic liquid without any intermediate mesophases (Fig. 1, Table I). Further curatives melt at the following temperatures: DCBS at ~ 95°C, stearic acid (SA) at ~ 64°C, and sulphur at ~ 124°C. ZnO does not show any changes in the given region.⁸

Information on the structure of the carboxylate groups of these systems was obtained from infrared and EPR spectra. The carboxylate ion may coordinate to a metal ion (M) by one of the following modes:¹³



Deacon and Phillips¹⁴ carried out many examinations of coordination of the carboxylate ion in many carboxylates having IR data and known X-ray crystal structures. They arrived at the conclusions that unidentate complexes (structure I) exhibit Δ values [asymmetric $\nu_{\text{as}}(\text{COO}^-)$ – symmetric $\nu_{\text{s}}(\text{COO}^-)$] much greater, while chelating (bidentate) complexes (structure II) significantly less, than the ionic values. The Δ values for the bridging complexes (structure III) are greater

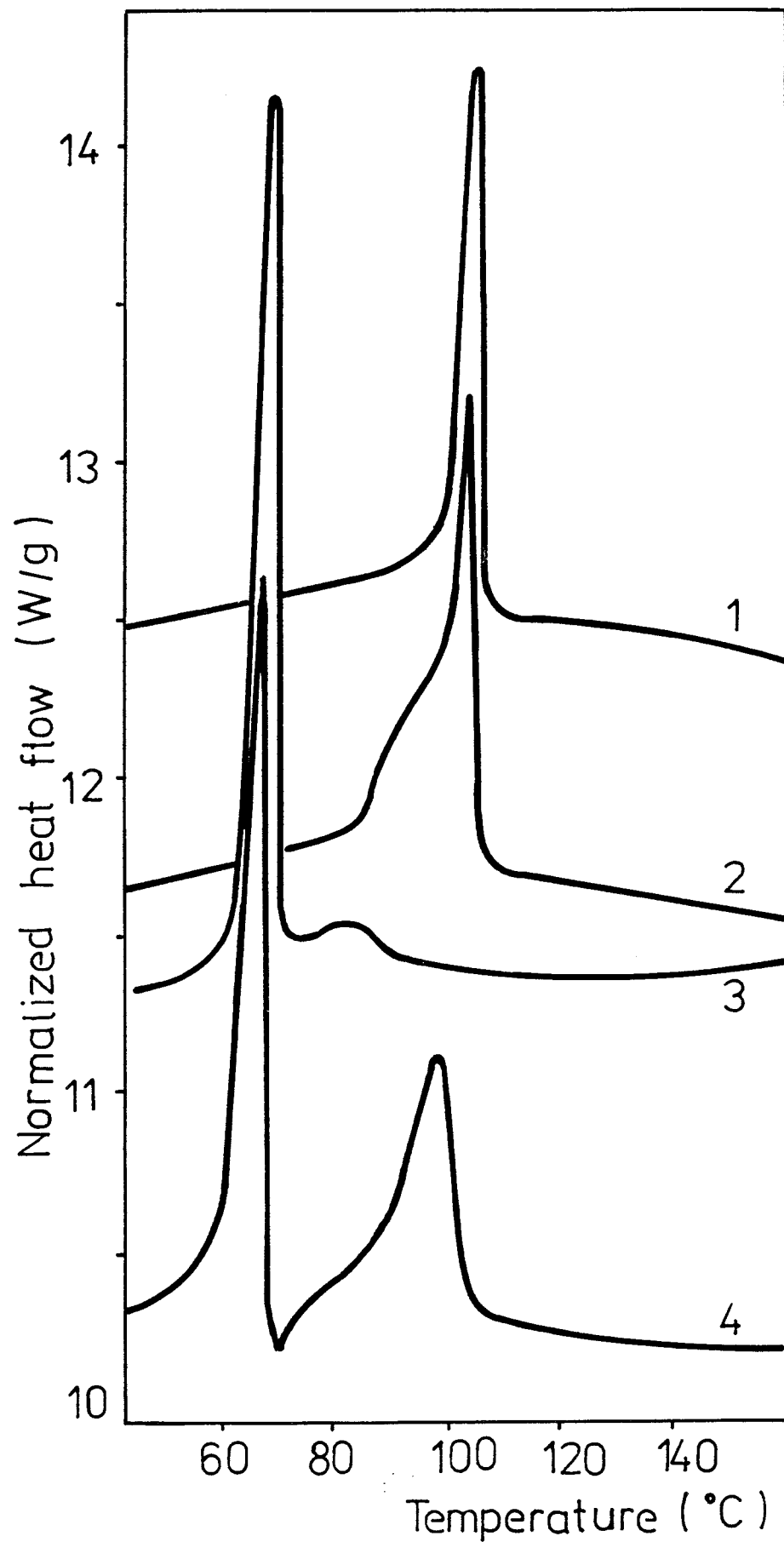


Figure 1 DSC curves of (1) CoC_{18} , (2) CoC_{18} + DCBS, (3) CoC_{18} + SA, (4) CoC_{18} + DCBS + SA.

Table I Peak Temperatures from DSC Measurements of the Studied Systems (20–160°C)

System	$T_{\max}/\pm 0.5^\circ\text{C}$		
DCBS	—	95,01	—
SA	63,6	—	—
S	—	—	123,9
ZnO	—	—	—
1. CoC ₁₈	—	104,5	—
2. CoC ₁₈ + DCBS	—	95(sh),104,3	—
3. CoC ₁₈ + SA	65,4	82,5	—
4. CoC ₁₈ + DCBS + SA	65,0	98,0	—
5. CoC ₁₈ + DCBS + SA + S	60,4	96,6	126,1
6. CoC ₁₈ + DCBS + SA + S + ZnO	57,5; 70, 100; ~ 105(sh)		124,2

sh—shoulder.

than those of the chelating complexes and less than the ionic values. Cobalt(II) stearate showed sharp asymmetrical [$\nu_{\text{as}}(\text{COO}^-) = \sim 1589 \text{ cm}^{-1}$] (Table II) and symmetrical vibrations [$\nu_{\text{s}}(\text{COO}^-) = \sim 1446\text{--}1412 \text{ cm}^{-1}$, mean value = 1440 cm^{-1}]. In the case of stearic acid the band near 1705 cm^{-1} is due to C=O stretching of acid groups. The values of ν_{as} vibration (and Δ) for Co(II) stearate are thus comparable to those of the bridging (polymeric) complexes, and stearate groups can be coordinated differently.

This is in agreement with literature data. For example, $\text{Co}(\text{C}_6\text{H}_5\text{COO})_2$ ¹⁵ consists of polymeric chains with octahedral coordination of Co(II)

(CoO₆), but benzoate ligands act differently. One benzoate group functions as a bridging ligand between adjacent metal atoms, the other acts as a fourdentate ligand by chelating one Co(II) atom and bridging its neighbors.

DSC and Spectral Studies of Complex Systems

The DSC thermogram of a mixture of CoC₁₈ and DCBS (Fig. 1) showed two thermal events. In addition to a relatively sharp peak at $\sim 104^\circ\text{C}$, a somewhat broad shoulder occurred at $\sim 95^\circ\text{C}$. When these results were compared with the thermograms of individual components, the change in

Table II Some Data of Infrared Spectra of the Carboxylic Groups (COO⁻) in the Studied Systems (1800–1500 cm⁻¹)

System	$t = 25^\circ\text{C}$			$t = 25^\circ\text{C} \rightarrow 140^\circ\text{C} \rightarrow 25^\circ\text{C}$			
	$\nu(\text{C}=\text{O})$	$\nu_{\text{as}}(\text{COO}^-)$		$\nu(\text{C}=\text{O})$	Other Vibrations		
Stearic acid (SA)	1705 (s)	—	—	1705 (s)	—	—	—
1. CoC ₁₈	—	1587 (s)	—	—	—	1571 (s)	—
2. CoC ₁₈ + DCBS	—	1589 (s)	—	—	1589 (w)	1570 (s)	1533 (w)
3. CoC ₁₈ + SA	1705 (s)	1589 (s)	—	1705 (s)	—	1568 (s)	—
4. CoC ₁₈ + DCBS + SA	1703 (s)	1591	—	1713 (s)	1598 (w)	1569 (s)	1530 (w)
5. CoC ₁₈ + DCBS + SA + S	1700 (s)	1591	—	1703 (s)	1601 (w)	—	1530 (s)
6. CoC ₁₈ + DCBS + SA + S + ZnO	1703 (s)	1587 (s)	—	1708 (w)	1593 (s)	—	1541 (vs)

[$\nu_{\text{as}}(\text{COO}^-)$ for ZnC₁₈ is 1540 cm^{-1}]⁸, (w—weak, s—strong, vs—very strong).

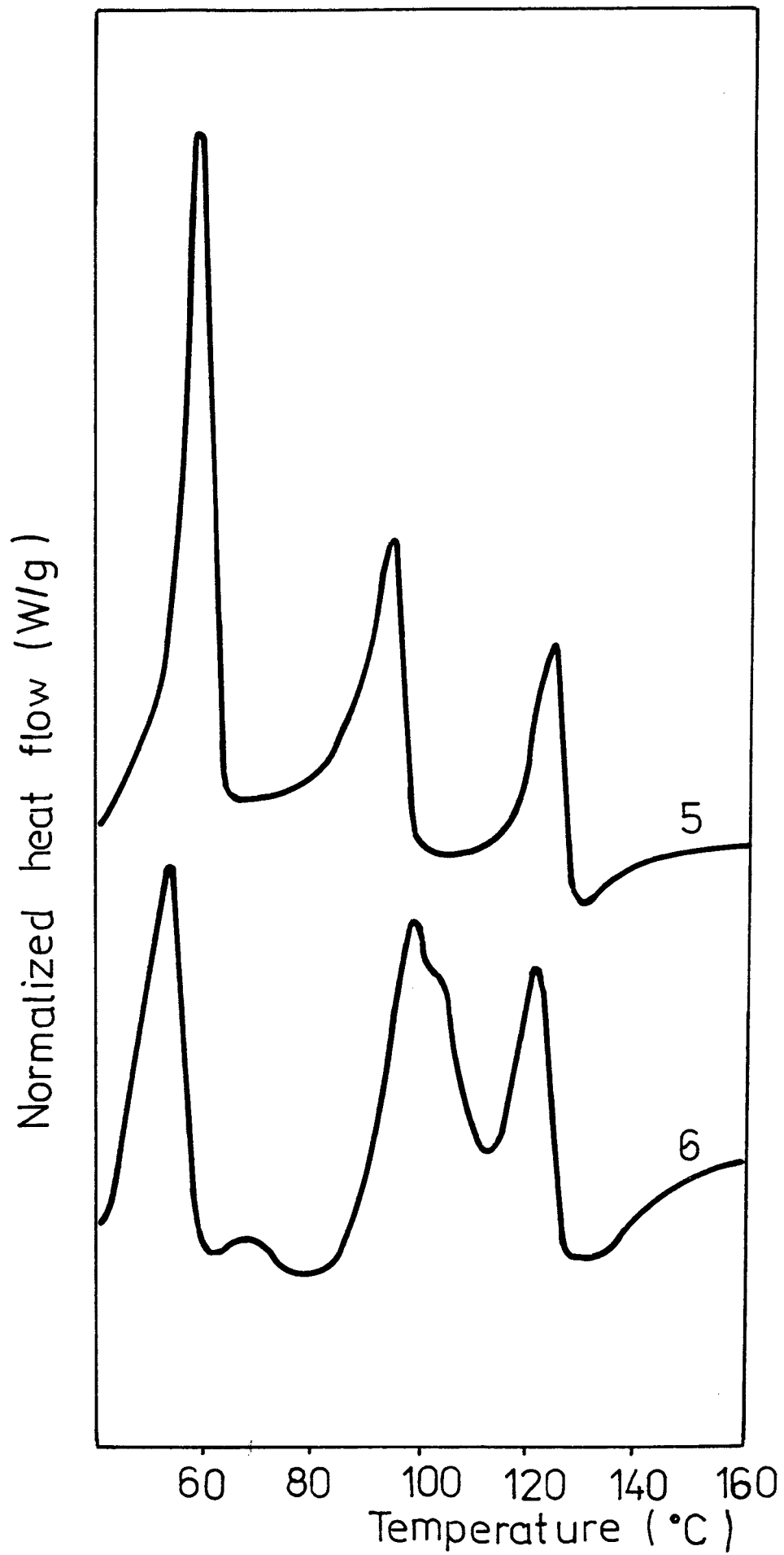
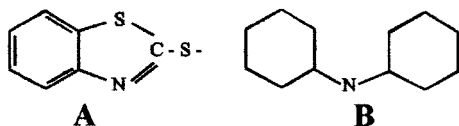


Figure 2 DSC curves of (5) $\text{CoC}_{18} + \text{DCBS} + \text{SA} + \text{S}$, (6) $\text{CoC}_{18} + \text{DCBS} + \text{SA} + \text{S} + \text{ZnO}$.

the shape and width of the peaks was observed. This fact indicated that these effects coincided with the melting and mutual interactions of the investigated components. The infrared spectrum obtained from this system was similar to those described for individual components at room temperature ($t = 25^\circ\text{C}$), but differed after heating. The bands near 1008, 1030, 1088, 1230, 1321, 1425, 1530, and 1598 were related to the benzothiazole fragments of DCBS.³ It is assumed that the first step of the mechanism may be the formation of DCBS fragments A and B:



CoC_{18} forms complexes with these fragments; however, the isolation of these complexes was not successful.

The DSC thermogram of the CoC_{18} -SA mixture was interpreted with reference to the previous spectra. Stearic acid melted at $\sim 65^\circ\text{C}$ (Table I, Fig. 1), while the weak endotherm observed at $\sim 83^\circ\text{C}$ could be attributed to the apparent melting and/or dissolution of CoC_{18} in molten stearic acid. The infrared spectrum of this system is similar to those described for individual components, especially $\nu_{\text{C}=\text{O}}$ stretching absorption at $\sim 1705\text{ cm}^{-1}$ (for SA) and $\nu_{\text{as}}(\text{COO}^-)$ at $\sim 1587\text{ cm}^{-1}$ at room temperature, and $\sim 1571\text{ cm}^{-1}$ after heating to 140°C and cooling down to room temperature (for CoC_{18}) (Table II).

The DSC thermogram of the CoC_{18} -DCBS-SA system obtained two endothermic peaks. Stearic acid melted at $\sim 65^\circ\text{C}$ and the peak at $\sim 98^\circ\text{C}$ is associated with the melting of DCBS, dissolution of CoC_{18} in DCBS and mutual interaction of the present components. The infrared spectrum is similar to the CoC_{18} -DCBS system with the exception of the presence of the $\nu_{\text{C}=\text{O}}$ absorption for SA.

In the presence of sulphur in four- and five-component systems (Fig. 2, Table I), the peak at the temperature exceeding 120°C occurs, which corresponds to the melting of sulphur. Because modification transitions of sulphur ($\text{S}_\alpha \rightarrow \text{S}_\beta$, $\text{S}_\beta \rightarrow \text{S}_\lambda$) do not appear separately in the thermograms, it may be considered that sulphur had undergone a reaction and was no longer present as sulphur-8 rings that could form polymeric sulphur.²

The absence of transition of sulphur may also indicate that sulphur had interacted with Co^{2+} ions and DCBS or DCBS fragments to form polysulfides or polysulfide complexes. Other effects in the four-component system ($\text{CoC}_{18} + \text{DCBS} + \text{SA} + \text{S}$) occurring below 120°C are due to the melting of SA (at $\sim 60,4^\circ\text{C}$) and melting and/or dissolution of CoC_{18} in molten stearic acid (at $\sim 96,6^\circ\text{C}$) (Table I). In the presence of ZnO in the five-component system the mutual interactions of the components present are different, and result predominantly in the formation of zinc(II) stearate by stearic acid reacting with ZnO.^{2,6-8} Then the effects on the DSC curve at ~ 70 , 100 , and $\sim 105^\circ\text{C}$ (Fig. 2) are evidently associated not only with the water evaporation, melting of DCBS, and CoC_{18} , but also with the melting of zinc(II) stearate.

The infrared spectra further showed that in the presence of sulphur in the four- and five-component systems, the band corresponding to the $\nu_{\text{as}}(\text{COO}^-)$ vibration of CoC_{18} has disappeared upon heating (Table II). Evidently, Co^{2+} ions form complexes with DCBS fragments and sulphur, as has been already stated.

This assertion is in agreement with the results of EPR spectra (Fig. 3). All EPR spectra are typical spectra for Co(II) in solid state with d^7 configuration. The EPR spectra of nonheated samples show, with the exception of the five-component system, a broad asymmetrical line with the effective value of the g factor $g_{\text{eff}} = 2233$. The five-component system shows an axially symmetric signal with $g_\perp = 1932$, $g_\parallel = 3342$. Thus, the presence of ZnO has a significant influence on magnetic properties of this system. EPR spectra of the heated two- and three-component systems show an approximately equal value of the g factor ($g_{\text{eff}} = 2235$). The difference has been observed in the systems with sulphur (Fig. 3), namely the appearance of a narrow line in the EPR spectra. It could be concluded that heating of four- and five-component systems led to a rearrangement of the CoC_{18} complexes with the participation of sulphur atoms.

CONCLUSIONS

The present article discusses a thermal and spectral study of the interactions between the curatives: dicyclohexylbenzothiazole-2-sulfenamide (DCBS), stearic acid (SA), zinc oxide (ZnO), and sulphur (S) with the participation of cobalt(II) octadecanoate (CoC_{18}) in the absence of rubber. Most thermal

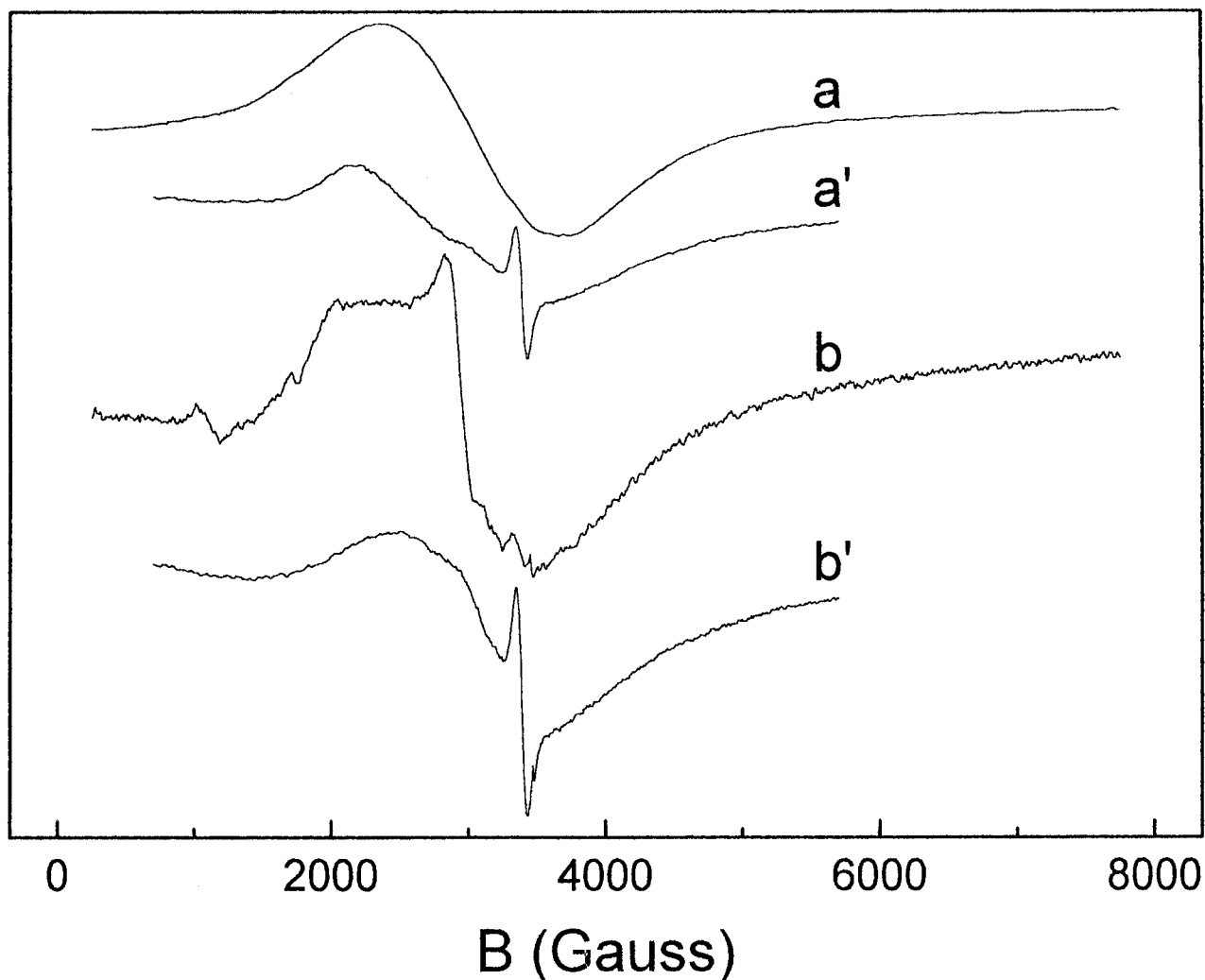


Figure 3 EPR spectra of (a) CoC_{18} + DCBS + SA + S (nonheated), (a') CoC_{18} + DCBS + SA + S (heated), (b) CoC_{18} + DCBS + SA + S + ZnO (nonheated), (b') CoC_{18} + DCBS + SA + S + ZnO (heated).

events could be associated with physical changes such as the melting of SA ($\sim 57\text{--}66^\circ\text{C}$), melting of DCBS together with the melting and/or dissolution of CoC_{18} ($\sim 82\text{--}105^\circ\text{C}$), and the melting of S ($\sim 123\text{--}126^\circ\text{C}$).

The prominent thermal reactions assumed were:

1. in the presence of CoC_{18} and DCBS: the formation of DCBS fragments, which may react with CoC_{18} on the action of heat;
2. in the presence of CoC_{18} , DCBS, and S: the formation of polysulfide complexes with Co^{2+} ions (released from CoC_{18}) and DCBS fragments;
3. in the presence of SA and ZnO: the formation of Zn(II) stearate, which is partly formed already after melting of SA.

The obtained results may contribute not only to the understanding of mutual interactions of the curatives but also to the role of the transition-metal ions in the vulcanization system.

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