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THERMOPARTICULATING ORGANIC COMPOUNDS

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The new technique of organoparticulate analysis has been used to investigate the thermal decomposition reactions of various types of organic compounds (i.e., metal acetylacetonates, blocked isocyanates, metal alkyldithiocarbamates, arenesulfonic acids and their amine salts). With a few exceptions, most of the compounds in these classes exhibit strong organoparticulation characteristics at temperatures below 200° as indicated by their influence on the output current of an ion chamber detector.

In general, no direct correlation between the melting and decomposition temperatures and their organoparticulation temperature ranges was evident. In several instances, the organoparticulation temperature range values lay well above or well beneath the known melting point and decomposition temperatures of the compounds.

To explain the organoparticulating properties of these compounds, vapor phase association of polar molecules (such as phenols, amines, carboxylic acids, etc.) would appear to be necessary to give organoparticulate sizes detectable with the present instrumentation. Alternatively, the formation of an "aerosol" suspension of organic molecules in gases, such as SO_2, CS_2, CO_2, might be occurring with some of these compounds.

Thermoparticulate analysis, which was used by Murphy and Doyle [1] for polymer degradation studies, is a technique based upon the detection of condensation nuclei evolved from polymer materials undergoing decomposition when subjected to programed heating. Recently, we have been successful in adapting this technique to follow the thermal decomposition of well-known organic compounds such as diazoniums [2] and malonic acids [3].

The new technique is termed organic particulate analysis [4] and enables a new physical property, namely, the temperature at which particulates are emitted from heated organic substances, to be measured. This analytical procedure makes it possible to detect the initiation of thermal decomposition at significantly lower temperatures than were previously assigned to such organic compounds [4]. In addition, the extreme sensitivity of the instrumentation used in this new technique has revealed that some of the organic compounds investigated are very strong sources of particulate emission, sometimes at temperatures well beneath their literature decomposition temperatures.

This paper serves to identify four new classes of organic compounds which have been found to exhibit these strong organoparticulation characteristics when subjected to programed heating. These new classes of compounds are as follows: 1) Metal acetylacetonates; 2) Arenesulfonic acids and their amine salts; 3) Blocked isocyanates; 4) Metal alkyldithiocarbamates.

As the results will show, *not* all of the compounds within these classes or "families" exhibit organoparticulation characteristics. However, the compounds that do, appear to have a common feature, i. e., they decompose at moderately low temperatures, produce polar gases or volatiles which are able to associate in the vapor phase to form particulates.

Experimental

The instrumentation used in these studies has been described previously [3–6]. The metal acetylacetonates and the metal dialkyl-dithiocarbamates were obtained commercially. The blocked isocyanates [7] and amine arenesulfonates [8] were prepared using standard synthetic procedures.

As described previously [3, 4] the various organic compounds under investigation were incorporated into a special air-drying epoxy polymer matrix which serves to prevent the compound from producing "dusting" during testing in the gas stream; this "dusting" effect could produce false particulate signals on the instrument (i. e., the particulates are not derived from decomposition of the organic compounds). The special polymeric expoxy material has been shown to particulate at temperatures well above (i. e., > 200°) that shown by the organic compounds under investigation. This ensured the minimum of interference from particulates derived from the epoxy matrix with those originating from decomposition of the organic compounds.

As in previous work [3], two temperatures were read from the recorder charts; the *threshold* temperatures which corresponded to the onset of organoparticulation (as shown by an initial fall-off in amplified ion current) and the temperature which signified a 50% decrease in the ion current (usually 0.8–0.4m A). These values enabled an "organoparticulation temperature range" to be determined for each sample.

Results and discussion

A typical ion chamber detector response is shown in Fig. 1 for cobalt(III) acetylacetonate. More detailed organoparticulation data are shown in Table 1 (metal acetylacetonates), Table 2 (arenesulfonic acids and their amine salts), Table 3 (blocked isocyanates), and Table 4 (metal alkyldithiocarbamates). Also included in these tables, for comparative purposes, are the melting points and decomposition temperatures for the various compounds.

Table 1

Metal acetylacetonate compounds

Sample No.	Metal acetylacetonate compound used	Organic particulation temperature range, °C	Literature melting point*, °C
SC-51/2	$Zn(C_5H_7O_2)_2 \cdot 2H_2O$	95–100	138
SC-60/2	$TiO(C_5H_7O_2)_2$	>190	>220
SC-80/6	$Al(C_5H_7O_2)_3$	159–161	189
SC-120/1	$Fe(C_5H_7O_2)_3$	171–174	179
SC-121/1	$Mg(C_5H_7O_2)_2$	>190	262–263
SC-164/1	$Mn(C_5H_7O_2)_2$	132–133	170
SC-165/1	$Co(C_5H_7O_2)_3$	128–131	100 (sublimes)
SC-166/1	$Co(C_5H_7O_2)_3$	150–152	240
SC-167/1	$Cu(C_5H_6O_2)_2 \cdot H_2O$	165–168	230–240(dec.)
SC-168/1	$Cr(C_5H_7O_2)_2$	179–183	214
SC-169/1	$Ni(C_5H_7O_2)_2 \cdot 2H_2O$	169–173	228
SC-182/1	$Mn(C_5H_7O_2)_2$	182–185	180
SC-240/1	$Zr(C_5H_7O_2)_4$	>190	171–173
SC-241/1	$Pb(C_5H_7O_2)_2$	147–152	145–163
SC-242/1	$Sr(C_5H_7O_2)_2$	>190	250 (dec.)

* Data supplied by Research Organic/Inorganic Chemical Co., Sun Valley, Ca.

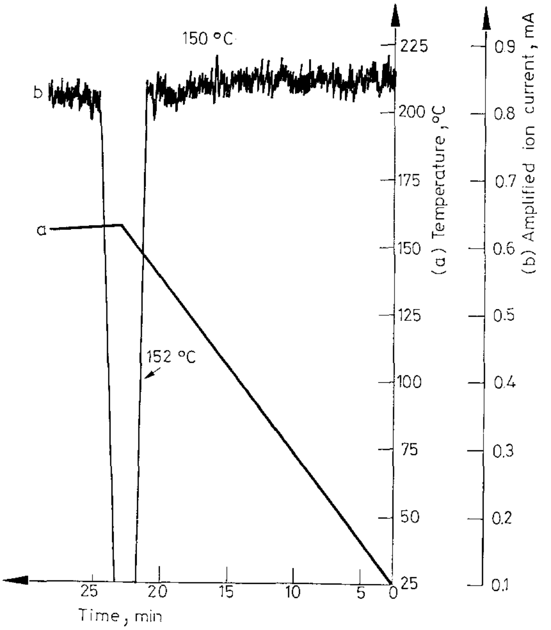


Fig. 1. Organoparticulation pattern for cobalt(III) acetylacetonate. Monitor: ion chambe detector; hydrogen flow rate: 6 l/min; heating rate: 6°/min.

Table 2

Arenesulfonic acids and amine salts

Sample No.	Sulfonic acid or amine sulfonate used	Organoparticulation temperature, °C	Literature melting point, °C
SC-193/1	p-Toluenesulfonic acid	115–119	103–106
SC-234/1	Benzenesulfonic acid	113–119	44–50
SC-235/1	3-pyridinesulfonic acid	177–187	>300
SC-236/1	1-naphthalenesulfonic acid	124–127	77–79
SC-270/1	Pyridinium benzenesulfonate	151–154	132–134*
SC-271/1	Morpholinium benzenesulfonate	184–188	110–112*
SC-272/1	*n*-butylamino benzenesulfonate	187–189	108–110*
SC-273/1	Morpholinium 3-pyridinesulfonate	>200	>230*
SC-94/1	Trimethylphenylammonium benzenesulfonate	>200	192–194*

* Obtained experimentally

Table 3

Blocked isocyanate organoparticulating compounds

Sample No.	Blocked isocyanate compound used	Organoparticulation temperature range, °C	Blocked isocyanate decomposition or melting point, °C[a]
SC-149/1	Hexamethylene diisocyanate + + dimethylamine	166–171	166–170
SC-151/1	Toluene diisocyanate + + mercaptobenzothiazole	161–165	153–161
SC-152/1	Toluene diisocyanate + + diethylamine	154–159	90–95
SC-150/1	Toluene diisocyanate + phenol	170–177	153–156
SC-180/1	Phenyl isocyanate + + dicyclopentenyl Alcohol	168–175	160–165
SC-183/1	Butyl isocyanate + 4,4'-Thiodiphenol	175–178	157–162
SC-161/1	Phenyl isocyanate + ethylmethyl ketoxime	169–173	126–130

[a] Obtained experimentally

It is evident from examining the data shown in these tables that, in general, there is no distinctive correlation between the organoparticulate temperature range values and the decomposition or melting points. In only a few instances (e. g., manganese(II) and lead(II) acetylacetonates in Table 2) do the values coincide. In most cases the onset of organoparticulation would appear to be *well above* or *beneath* the literature values.

It has been established previously [2, 3] that a critical *minimum size* particulate is required to register a signal on the ion chamber detector. This critical size is of the order 25 Å, suggesting that vapor phase association of volatile decomposition products would be necessary to give the required dimensions.

Using a representative cross-section of the organoparticulating compounds shown in Tables 1–4 as examples, (i. e., toluene diisocyanate/diethylamine product, cadmium diethyldithiocarbamate, cobalt(III) acetylacetonate and pyridinium *p*-toluene sulfonate), the anticipated decomposition products from these materials would be as follows:

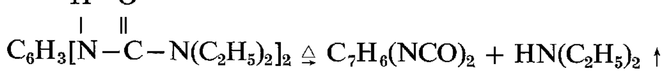
Table 4

Metal alkyldithiocarbamate compounds

Sample No.	Metal alkyldithiocarbamate compound used	Commercial trade-name	Organoparticulating temperature range, °C	Literature decomposition or melting point, °C
SC-111/1	Cadmium diethyldithiocarbamate	Cadmate or ethyl Cadmate	159–165	68– 76
SC-112/1	Tellurium diethyldithiocarbamate	Tellurac	157–162	108–118
SC-113/1	Lead dimethyldithiocarbamate	Ledate	>190	>310
SC-114/1	Copper dimethyldithiocarbamate	Cumate	>190	>324
SC-115/1	Zinc diethyldithiocarbamate	Ethazate	>190	173–178
SC-116/1	Bismuth diethyldithiocarbamate	Bismate	>190	230
SC-117/1	Selenium diethyldithiocarbamate	Ethyl selenac	160–209	59– 85
SC-118/1	Zinc dibutyldithiocarbamate	Butuzate or Butyl zimate	184–190	104
SC-119/1	Zinc dimethyldithiocarbamate	Methyl zimate	>190	242–257

[a] Values from Rubber Blue Book, "Materials & Compounding Ingredients for Rubber" pp. 31–61 (1975).

1. Toluene diisocyanate-diethylamine product

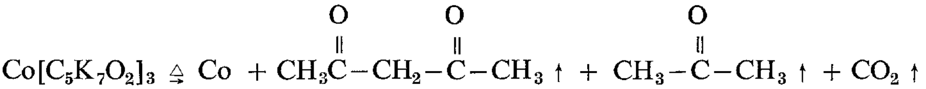


$$\mathrm{C_6H_3[\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2]_2 \overset{\triangle}{\rightarrow} C_7H_6(NCO)_2 + HN(C_2H_5)_2\uparrow}$$

2. Cadmium diethyldithiocarbamate

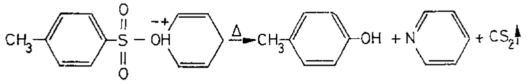
$$\mathrm{Cd^{2+}[S-\underset{\underset{S}{\|}}{C}-N(C_2H_5)_2]_2 \overset{\triangle}{\rightarrow} Cd[N(C_2H_5)_2]_2 + CS_2\uparrow}$$

3. Cobalt(III) acetylacetonate



$$\mathrm{Co[C_5K_7O_2]_3} \overset{\Delta}{\rightarrow} \mathrm{Co} + \mathrm{CH_3\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3}\uparrow + \mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}\uparrow + \mathrm{CO_2}\uparrow$$

4. Pyridinium p-toluene sulfonate



The decomposition products shown above are somewhat simplified since further decomposition of the non-volatile species can also occur. However, the anticipated volatiles derived from these compounds (indicated ↑) are, in general, of a polar nature. Some, such as $NH(C_2H_5)_2$, would be extremely polar. Thus, vapor phase association of these polar materials would be extremely likely to give H-bonded oligomers of the dimensions required to register a response on the ion chamber detector. The formation of an "aerosol" suspension of polar organic material in a gaseous atmosphere (CO_2, SO_2, and CS_2) could also give rise to the required particulate size. Such polar organic materials might be phenols (derived from the amine p-toluene sulfonates), amines (derived from the blocked isocyanates and metal dialkyldithiocarbamates), and acetylacetone (derived from metal acetylacetonates).

Mass spectral studies have been carried out with vapor phase effluents derived from some of the organoparticulation compounds [2, 3, 9, 10] and species akin to the ones outlined above have been positively identified. However, further work remains to be done in characterizing the actual nature of these organoparticulates. These characterization studies are somewhat hampered because of the lower sensitivities of the "back-up" instrumentation, such as gas chromatography and mass spectrometry, compared to the ion chamber detector. Also, the lifetimes of "trapped" organoparticulate species are of uncertain duration and by the time the characterization studies have been carried out, the nature of the particulates may have changed.

Further characterization studies on the organoparticulates derived from the compounds described in this paper and also on others are being carried out and will be reported in future papers in this area.

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Résumé — Application de la nouvelle technique d'analyse des particules organiques à l'étude des réactions de décomposition thermique de divers types de composés organiques (par ex. les acétylacétonates métalliques, les isocyanates bloqués, les alkyldithiocarbamates métalliques, les acides arénosulfoniques et leurs sels aminés). A quelques exceptions près, la plupart des composés de ces différentes classes montrent de fortes caractéristiques d'organoparticulation aux températures inférieures à 200°, qui se manifestent par leur influence sur le courant de sortie d'un détecteur à chambre d'ions.

Il n'a pas été possible, en général, de mettre en évidence une corrélation directe entre les températures de fusion et de décomposition et les intervalles des températures de l'organoparticulation des composés. Dans plusieurs cas, les valeurs de l'intervalle des températures d'organoparticulation étaient nettement supérieures ou nettement inférieures au point de fusion connu et aux températures de décomposition des composés.

Afin d'expliquer les propriétés d'organoparticulation de ces composés, l'association en phase vapeur de molécules polaires (par ex. les phénols, les amines, les acides carboxyliques, etc.) semble être nécessaire pour donner des organoparticules de grandeur décelable par les instruments actuels. Une autre possibilité serait la formation d'une suspension "aérosol" de molécules organiques dans des gaz comme SO_2, CS_2, CO_2, qui pourrait se produire avec quelques-uns de ces composés.

Zusammenfassung — Die neue Technik der organischen Partikelanalyse wurde zur Untersuchung der thermischen Zersetzungsreaktionen verschiedener Typen organischer Verbindungen (z. B. Metall-Acetylacetonate, blockierte Isocyanate, Metall-Alkyldithiocarbamate, Arensulfonsäuren und ihre Aminsalze) eingesetzt. Mit einigen Ausnahmen weist der Grossteil dieser Verbindungsklassen starke, bei Temperaturen unter 200° organische Partikelcharakteristika auf, wie an Hand ihrer Wirkung auf den austretenden Strom eines Ionenkammerdetektors nachgewiesen werden kann.

Im Allgemeinen konnte kein direkter Zusammenhang zwischen den Schmelz- und Zersetzungstemperaturen und den Temperaturbereichen der Organopartikulierung der Verbindungen festgestellt werden. In mehreren Fällen lagen die Temperaturbereiche der Organopartikulierung deutlich oberhalb oder unterhalb des bekannten Schmelzpunktes und der Zersetzungstemperaturen der Verbindungen.

Um die organopartikulierenden Eigenschaften dieser Verbindungen zu erklären, scheint eine Dampfphasenassoziierung polarer Moleküle (wie z. B. Phenole, Amine, Carbonsäuren, usw.) nötig um mit der derzeitigen Instrumentierung nachweisbare Partikelgrössen zu ergeben. Als andere Möglichkeit könnte die Bildung einer "Aerosol"-Suspension organischer Moleküle in Gasen (wie z. B. SO_2, CS_2, CO_2) bei einigen dieser Verbindungen gesehen werden.

Резюме — Новая техника анализа органо-частиц была использована для изучения реакций термического разложения различных типов органических соединений (например, ацетилацетонатов металлов, блокированных изоцианатов, металл-алкилдитиокарбаматов, аренсульфокислот и их аминосолей). За несколькими исключениями, большинство соединений в этих классах проявляет сильные характеристики органо-частиц при температурах ниже 200°C, что установлено их влиянием на выходной ток какого-либо ион-камерного детектора. В общем, было очевидно, что нет прямой корреляции между температурами плавления, разложения и температурами образования их органо-частиц. В нескольких сучаях область температур образования органо-частиц лежит как выше, так и ниже известных точек плавления и температур разложения этих соединений. Для объяснения свойств образования органо-частиц этими соединениями, повидимому, должна быть необходимой парофазная ассоциация полярных молекул (таких как фенолы, амины, карбоновые кислоты и т. д.), чтобы дать соответствующие размеры органо-частиц, обнаруживаемых настоящей техникой. Альтернативно, образование какой-либо «аэрозольной» суспензии органических молекул в таких газах как SO_2, CS_2, CO_2, может происходить с некоторыми из этих соединений.