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INVESTIGATION OF COMPLETE OXIDATION OF ORGANIC MATERIALS WITH THERMAL ANALYTICAL MEASUREMENTS

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The complete oxidation of styrene–divinylbenzene has been examined with complex thermoanalytical methods by derivatograph and thermogastitrimeter. With the combined application of combustion catalyst and postcatalytic method the oxidation of the styrene–divinylbenzene is complete.

The oxidation of organic materials, i.e. the conversion of the organic carbon content into carbon dioxide, can be improved by the use of oxygen atmosphere at 900–1000° [1], and/or by means of so-called combustion catalysts (like copper oxide) [2]. The catalysts usually not only increase the rate of conversion, but reduce the oxidation temperature as well. The current CHN-analyzers utilize these methods in due sequence [3].

An earlier paper reported on the oxidation of different organic substances while recording thermoanalytical curves by derivatograph [2]. The carbon dioxide evolved was simultaneously determined by gastitrimetric method [4] (by continuous alcalimetric titration). Using oxygen gas atmosphere and some metal oxide catalysts, and certain optimal conditions (heating rate, sample preparation, crucible etc.) the oxidation of saccharose and gelatine was complete, but difficulties arose at the thermal oxidation of styrene–divinylbenzene copolymer samples.

The present paper describes the complete oxidation of a styrene-divinylbenzene copolymer (SDVB) sample using a postcatalytic method.

The thermal analysis using derivatograph was carried out the usual way. To the end of the gas collector, however a glastube was inserted, in which a platinum spiral (0.25 mm diameter, 55 cm long) was heated to red hot (with 3.5 A current intensity) during the entire operation. The combustion product was sucked via the red heat platinum spiral into the absorbers of the attached gas titrimeter, and the carbon dioxide absorbed in the first absorber titrating vessel was simultaneously titrated.

It was found that using oxygen gas atmosphere and metal oxide catalyst in the crucible, and the postcatalytic combustion spiral, the combustion of the SDVB sample was complete and the evolved, absorbed and titrated carbon dioxide corresponded with the expected value.

Experimental

Materials

Styrene–divinylbenzene copolymer beads (330 mesh). The carbon content of the copolymer was determined by the classical combustion method and found to be 83.6%.

Coboxide (combustion catalyst of Perkin–Elmer, Maywood Ill. USA). Aluminium oxide (anal. q.).

Instruments

Derivatograph (MOM, Hungary) was used for the thermal treatment of the sample and of the mixtures. The sample (mixture) was placed in a perforated platinum crucible, and through the gas collecting adapter the carrier oxygen gas was sucked into the absorbers of the Thermogastitrimeter (MOM, Hungary).

Procedure

20.0 mg SDVB sample alone or mixed with finely powdered 100 mg Coboxide and with 120 mg aluminium oxide was weighed into the perforated platinum crucible of the derivatograph. During the programmed continuous heating from ambient up to 600° the content of the CO_2 evolved was continuously titrated and registered by the thermogastitrimeter. When the postcatalytic method was applied the combustion products were sucked via the platinum spiral heated to red hot before leaving into the absorbers of the gas titrimeter.

During the entire operation 25–30 l/h oxygen input flow rate and 10 l/h suction flow rate were maintained.

The quantity of the CO_2 was determined by 0.1 *N* NaOH as titrant at 9.3 pH. Known amount of $KHCO_3$ was used to calibrate the gas collecting system and to standardize the titrant.

Weighing 200 mg $KHCO_3$ into the crucible the standard deviation of CO_2-determination was 1.1%.

Results

The thermogastitrimetric curves TGT curves of styrene–divinylbenzene and that of its mixture with Coboxide are presented in Figs 1 and 2 resp. The results calculated from the thermogastitrimetric curves are summarized in Table 1. All data shown in Table 1 were obtained as the results of the averages of three parallel thermogastitrimetric titrations.

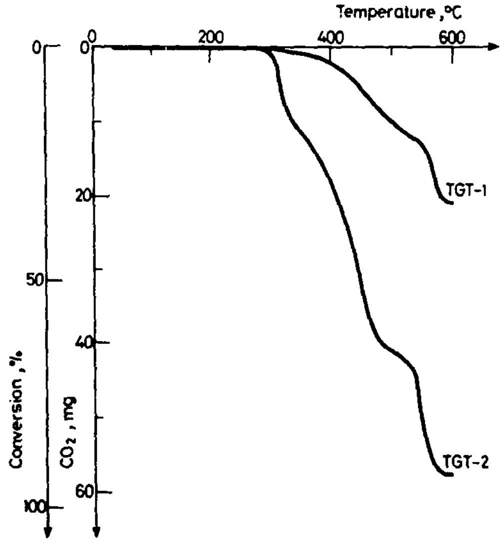

Fig. 1 Thermogastitrimetric curves of styrene–divinylbenzene (SDVB). 1 – Titration curve, taken from the thermal decomposition of 20 mg SDVB in oxygen atmosphere under usual conditions, 2 – Titration curve, taken from the thermal decomposition of 20 mg SDVB in oxygen atmosphere. The combustion products were led via red hot Pt-spiral

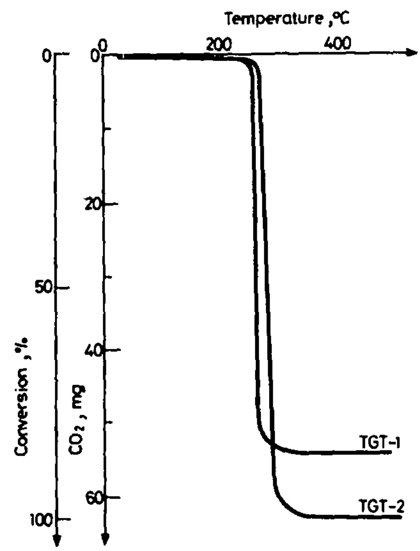

Fig. 2 Thermogastitrimetric curves of styrene–divinylbenzene mixed with combustion catalyst: Coboxide. 1 – Titration curve taken from the thermal decomposition of 20 mg SDVB + 100 mg Coboxide + 120 mg Al_2O_3 in oxygen atmosphere under usual conditions. 2 – Titration curve taken from the thermal decomposition of 20 mg SDVB + 100 mg Coboxide + 120 mg Al_2O_3. The combustion products were led via red hot Pt-spiral

Table 1 Determination of the carbon-dioxide content of combustion products of styrene-divinylbenzene (SDVB) in oxygen atmosphere by thermogastitrimetric method under different conditions

Sample weight	Conditions	CO_2 content, mg calcd.,	found,	Conversion, %
	–	61.3	19.6	32
20.0 mg SDVB	using red hot			
	Pt-spiral	61.3	57.0	93
20.0 mg SDVB +	–	61.3	53.3	87
100 mg Coboxide +	using red hot			
120 mg Al_2O_3	Pt-spiral	61.3	61.9	101

Discussion

The styrene–divinylbenzene copolymer is difficult to oxidize during the conventional thermal analytical conditions. Only one third of its carbon content converses to carbon dioxide even in oxygen atmosphere. Not even the addition of a combustion catalyst can lead to adequate results. With application of both combustion catalyst and postcatalytic method, however, the complete oxidation of carbon content of the copolymer can be ensured (Table 1): the conversion of carbon content to carbon dioxide is complete.

References

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Zusammenfassung — Die vollständige Oxydation von Styrol—Divinylbenzol wurde mittels einer komplexen thermoanalytischen Methode unter Verwendung eines mit einem Gastitrimeter kombinierten Derivatographen untersucht. Eine vollständige Oxydation wird bei Anwendung eines Verbrennungskatalysators und der postkatalytischen Methode erreicht.

Резюме — Полное окисление стирол-дивинилбензола было исследовано с помощью дериватографа и термогазотитриметрии. Окисление происходит польностью при использовании каталитического сжигания и последующего за ним сжигания.