Incremental Modification of Styrene–Butadiene Rubber with *tert*-Nonyl Mercaptan

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Synopsis

A model equation derived for the viscosity-average degree of polymerization ($\bar{P}_v$) for the incremental addition of modifiers, $\bar{P}_v = K\{(\exp\{arx_1\} - 1) + [2/(2 + \exp\{x_1r\})]^a (\exp\{arx_2\} - \exp\{arx_1\})\}^{1/a}$ indicates a minimum should occur in a curve of $\bar{P}_v$ versus conversion at which the increments are added, x_1. Incremental addition of commercial *tert*-dodecyl mercaptan in the laboratory to SBR recipes at 5°C. showed effects contrary to those predicted by the model equation, but incremental addition experiments with *tert*-nonyl mercaptans resulted in a minimum in viscosity versus x_1 curves, changed the molecular weight distribution, and required 34 wt.-% less mercaptan than did the *tert*-dodecyl mercaptan control (all the *tert*-dodecyl mercaptan added initially). Incremental addition of *tert*-nonylmercaptan in pilot plant 20-gal. autoclave reactors gave essentially the same results found in the laboratory bottle experiments. The stress–strain and mixing properties of the incrementally modified polymer and the *tert*-dodecyl mercaptan-modified control were essentially the same within experimental error. Conditions required for successful application of the incremental modifier technique are given.

INTRODUCTION

Modification by continuous or incremental addition of mercaptans during polymerization in emulsion systems has long been studied in the synthetic rubber industry.[1-3] The procedure was expected to have one or more of the following effects: produce uniform viscosity polymer during the course of polymerization, narrow or change the molecular weight distribution, or lower mercaptan requirements. In the Mutual recipe (50°C. polymerization) the incremental procedure did lead to uniform viscosity during polymerization and lower mercaptan requirements, but molecular weight distribution was not significantly changed.[2] In one low temperature recipe, the only advantage gained by use of an incremental procedure was uniform viscosity during polymerization.[3]

The present report describes successful modification by incremental addition of mercaptan in low temperature recipes (5°C. polymerization). A model equation, which will be the subject of another report, for viscosity-average degree of polymerization $\bar{P}_v$ of a polymer prepared by the addition of two increments is:

$$\bar{P}_v = k\left[\frac{M_0}{S_0}\right]\left(\frac{1}{x_2 ar^{1+a}}\right)^{1/a}\left\{(e^{arx_1} - 1) + \left(\frac{2}{2 + e^{x_1r}}\right)^a (e^{arx_2} - e^{arx_1})\right\}^{1/a} \qquad (1)$$

where $[M_0]$ and $[S_0]$ are the original monomer and modifier concentrations, respectively, r is the mercaptan regulating index, a is the exponent in the Mark-Houwink equation, x_1 is the fractional conversion at which increment is added, x_2 is final conversion, and 2 is the ratio of initial to final increment. Since the values to the left of the braces are constants for any single polymerization, the shape of a curve for $\bar{P}_v$ versus x_1 will be determined by the braced function. The shape of the $\bar{P}_v$ versus x_1 curve when $a = 0.5$, $r = 3$, $x_2 = 0.6$, and x_1 varies from zero to 0.6 is shown in Figure 1.
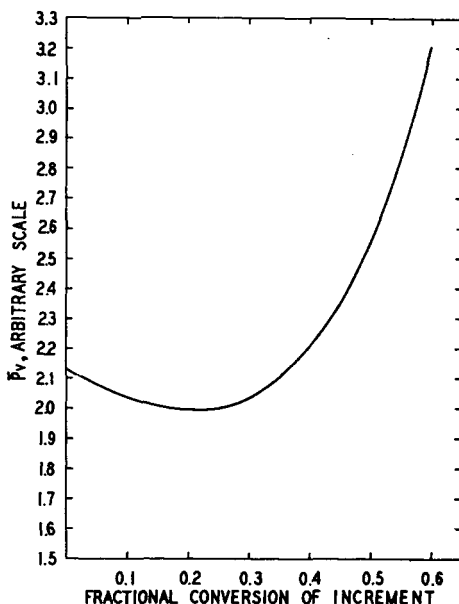

Fig. 1. Degree of polymerization vs. conversion of incremental addition of mercaptan.

This curve indicates that any viscoelastic property that is a function of $\bar{P}_v$ should exhibit a minimum in a viscoelastic property-conversion at incremental addition curve. Likewise, the minimum indicates lower mercaptan requirements for the incremental addition procedure. However, when *tert*-dodecyl mercaptans commonly used as modifiers were added in several portions to a 5°C. sulfoxylate recipe[4] in laboratory experiments, none of the preceding predicted results were obtained. On the contrary, the Mooney viscosities and dilute solution viscosities of the polymers prepared by the incremental addition of *tert*-dodecyl mercaptans were considerably higher than those of the control polymer when all the mercaptan was added initially. The experiments performed in the present study are described in the following sections.

EXPERIMENTAL PROCEDURE

Polymerization Recipe and Procedures

A standard butadiene–styrene, sulfoxylate, 5°C. SBR-1502 type of recipe[4] was used in the laboratory part of this study and the SBR-1500 recipe[4] was used to prepare an evaluation sample in the pilot plant. The bottle polymerization technique was employed.[5] In the normal charging procedure all the mercaptan was added in the styrene. In the incremental technique, two-thirds of the mercaptan was added originally in the styrene and the increment was added by syringe during the course of the polymerization as a solution in benzene, or as an emulsion. All concentrations of mercaptans are expressed in this report as phm, parts per hundred monomer.

Mooney Viscosity and Inherent Viscosity Determination

The ASTM standard procedure[6a] was employed for Mooney viscosities, and inherent viscosities were determined in Medalia viscometers[7] with toluene solutions.

Polymer Fractionation

The Baker-Williams column technique[8] was scaled up to handle 1.0 g. of polymer. The fractionation required approximately 3 days and isolation and viscosity measurements approximately 2 days more. The fractions exhibited a reversion which is commonly encountered with diene polymers by this fractionation procedure.[10]

Mercaptans

The $tert$-dodecyl mercaptan (t-$C_{12}SH$) was Sulfole B-8 mercaptan (Phillips Petroleum Co. trademark) which was >96 + wt.-% mercaptan. The $tert$-t-nonyl mercaptan (t-C_9SH) (Phillips) was >97 + wt.-% mercaptan.

Ultracentrifugation

Polymer solutions in n-heptane were examined in a Spinco analytical ultracentrifuge. Qualitative comparisons of the Schlieren patterns were made.

EXPERIMENTAL RESULTS

Inherent in any free radical polymerization of dienes are branching and crosslinking reactions which produce discontinuities in some polymer properties.[9] It is advisable in incremental addition experiments with diene systems to add the amounts of the increments so that crosslinking does not occur between additions. For this reason in all the following incremental addition experiments, the mercaptan was divided into two portions, two-

thirds of the mercaptans was added initially and one-third at a higher conversion.

Incremental Addition of *tert*-Dodecyl Mercaptan

Typical results obtained for a series of incremental additions of Sulfole mercaptan for which the second increments were added at different conversions are shown by Figure 2A. Each point of the curve represents a single run in which two-thirds of the mercaptan was added initially, one-third was added at an intermediate conversion, polymerization was terminated at 60% and Mooney determined at this conversion. Several variations of this incremental addition experiment were tried: different incremental ratios, addition of the second increment in different solvents, substitution of methanol for some of the water, and addition of the increment as a soap emulsion. Although no useful advantage was gained by adding the *tert*-dodecyl mercaptan using these variations, the shape of the Mooney versus conversion for increment curve was sometimes changed, as in the experiment when the increment was added in an émulsion (Fig. 2B).
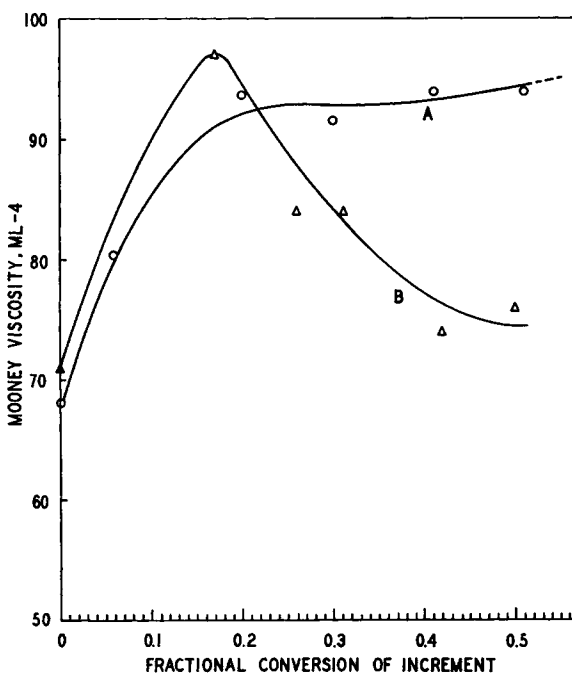

Fig. 2. Mooney viscosity vs. conversion of *tert*-dodecyl mercaptan increment: (A) in benzene; (B) as an emulsion.

Incremental Addition of *tert*-Nonyl Mercaptan

tert-Nonyl is a more efficient modifier than *tert*-dodecyl mercaptan when all the modifier is added originally as is shown in Table I. The marked

TABLE I
Polymerization Data for Controls and Incremental Addition of *tert*-Nonyl Mercaptan

Charge order	Control		Increment *t*-C₉SH
	Sulfole	*t*-C₉SH	
Initial, phm	0.216	0.179	0.095
Increment, phm	—	—	0.047
Total, phm	0.216	0.179	0.142
Mooney at 60%, ML-4	54	46	46
Saving, wt.-% of *t*-C₁₂SH	—	17	34

effect on Mooney and on inherent viscosity of incremental addition of *tert*-nonyl mercaptan at different conversions is shown in Figure 3.

In addition to the pronounced effect incremental addition of *tert*-nonyl mercaptan has on Mooney viscosity, other polymer characteristics are also affected.   Figure 4 shows results for the inherent viscosity of polymers from one incremental addition experiment sampled at different conversions. Figure 4 shows both a delay in the decrease of inherent viscosity after the increment was added and a minimum before the polymerization was terminated.

The molecular weight distributions for a *tert*-nonyl mercaptan-modified control and for the incremental polymer with the same Mooney viscosity
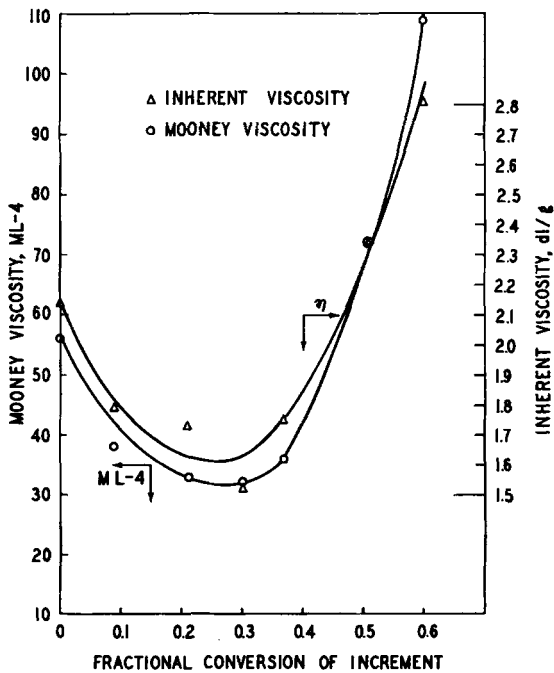

Fig. 3. Mooney and inherent viscosities vs. conversion for increment of *tert*-nonyl mercaptan.

were obtained (Fig. 5). Although the breadth of the molecular weight distribution is the same for the two, the distribution is obviously different. Examination of the control and experimental polymer by ultracentrifugation indicated a narrower distribution for the polymer prepared by the incremental technique. However the Schlieren pattern for both polymers showed only one peak. More work on the molecular weight distribution needs to be done.

The greater efficiency of modification obtained by incremental addition of *tert*-nonyl mercaptan should be reflected in a lower mercaptan require-
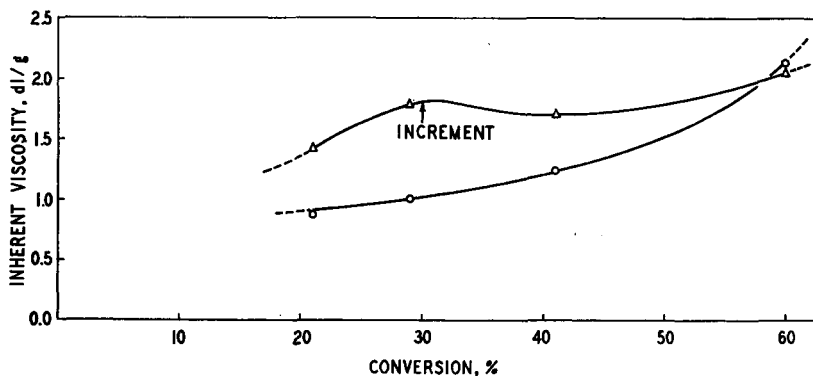

Fig. 4. Inherent viscosity vs. conversion: (O) 0.179 phm t-C_9SH added initially; (Δ) 0.095 phm t-C_9SH added initially and 0.047 phm at 30% conversion.
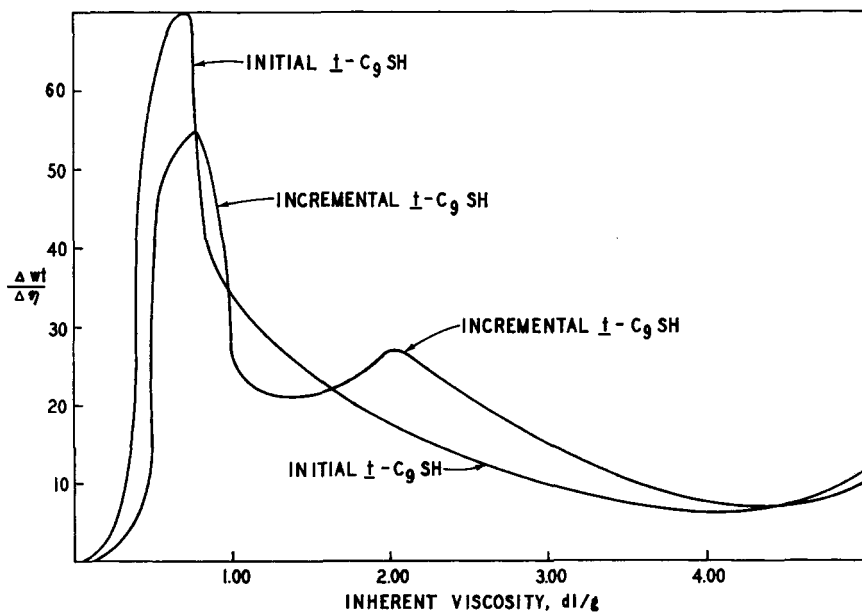

Fig. 5. Molecular weight distribution for polymer modified by all *tert*-nonyl mercaptan added initially and by *tert*-nonyl mercaptan added in two increments.

ment for production of a standard Mooney polymer.   The data in Table I show the efficiency in comparisons with *tert*-nonyl and *tert*-dodecyl mercaptan controls.

Similar savings were found in the pilot plant for incremental addition polymerizations conducted in autoclave reactors (Table II).

Physical Properties of Vulcanizates of Polymers Prepared by Incremental Addition of *tert*-Nonyl Mercaptan

A Sulfole mercaptan control and incremental *tert*-nonyl mercaptan modified polymers were prepared in the pilot plant 20-gal. reactors in ac-

TABLE II
Polymerization Data for Control and Incremental Addition SBR-1500 Copolymers

	Sulfole mercaptan, control	t-C_9SH mercaptan, increment
Initial mercaptan, phm	0.22	0.0993
Increment mercaptan, phm	—	0.0497
Total mercaptan, phm	0.22	0.1490
Saving, % of t-$C_{12}SH$	—	32
Conversion, %	62	60
Time, hr.	10.6	9.6
Inherent viscosity	2.00	2.15
Mooney viscosity, ML-4	53	56
Acid, %	5.7	6.6

TABLE III
Physical Properties for Control and Incremental t-C_9SH SBR-1500 Copolymers[a]

	Sulfole mercaptan, control	t-C_9SH mercaptan, increment
$\nu \times 10^4$, moles/cc.	1.22	1.22
300% modulus, psi		
25 min. cure	300	350
50 min. cure	1000	1100
100 min. cure	1400	1450
Tensile strength, psi	4300	4100
Elongation, %	680	630
Compound Mooney, ML-4[b]	60	62
3 min. Mixing Time[b]		
Total Power, w-hr.	174	192
Dump temperature, °F.	240	245
Mooney, ML-4	47	54
10 min. mixing time[b]		
Total power, w.-hr.	498	546
Dump temperature, °F.	260	265
Mooney, ML-4	47	49

[a] Cure 50 min. at 292°F. unless otherwise noted.
[b] Raw polymer mixing study.

cordance with a SBR-1500 recipe.[4]   The polymerization data are given in Table II and the physical properties of the vulcanizates[6b] are in Table III.

The stress–strain and mixing properties of the two polymers are within experimental error essentially the same in the compounding recipe employed.   Similarly the polymers prepared in the laboratory in bottles with the two mercaptans by the different procedures showed essentially no difference in stress–strain properties in the same recipe as employed above.

For other applications the polymers should be evaluated in appropriate compounding recipes.

DISCUSSION

The model equation, eq. (1), fulfills some of the tests of a valid equation. When boundary conditions are applied, e.g., all mercaptan added initially and no increment or a portion added initially and the increment added at terminal conversion, the equation remaining, except for a constant, is identical to that derived for the case when all mercaptan is charged initially,[11] as should be expected.   The simulated curve exhibits a minimum, and the equation is differentiable with respect to x_1.   The calculated minimum value for x_1 using the values for Figure 1 is approximately 0.2.   However, the most significant test of the equation is the minimum in viscosities found for the experimental curves (Fig. 3) with tert-nonyl mercaptan.

The difference in the results obtained with tert-dodecyl and tert-nonyl mercaptans when added in increments may be attributable to the marked differences in the rates of transfer of the mercaptans from the monomer to the particle phase.   Many workers have studied the effect of molecular weight of a homologous series of mercaptan on modification in emulsion polymerization systems.[5,12−14]   When the molecular weight of the mercaptan is high, an equilibrium distribution of mercaptan between monomer and particle phases is not attained, and the concentration of the mercaptan at the site of polymerization is lowered.   Under these conditions an apparent distribution of mercaptan between phases must exist, and mercaptan depletion measurements give apparent regulating indices.   No studies have been made on the rate of attainment of equilibrium distribution of mercaptans in incremental addition procedures.   If the attainment of an equilibrium distribution of the increment is greatly delayed because of the size of the mercaptans, the effectiveness of the increment is greatly reduced.   Under these circumstances, incremental addition can be less effective than adding all mercaptan originally.   This is a possible explanation for the difference in behavior between tert-dodecyl and tert-nonyl mercaptans in the systems studied.

The inherent viscosity–conversion curve (Fig. 4) indicates a constant viscosity during polymerization would be readily attained if several increments were added during the course of polymerization.   However, the model equation derived for the addition of three increments shows only a slightly more overall effective utilization of mercaptan than does the case

of adding only two increments.   The big jump in effectiveness of the incremental procedure is found when the mercaptan is divided into two portions.

Fractionation of the control and incremental polymer showed little difference in the breadth of the molecular weight range; however, a difference in the distribution was apparent (Fig. 5).   Calculations of a heterogeneity index, $\bar{M}_w/\bar{M}_n$, using model equations give values of 2.60 for all mercaptan added initially and 2.14 for the incremental case.   The same values calculated with the data employed for the curve of Figure 5 were 3.03 and 2.06, respectively.   Although the latter values are invalidated somewhat by the reversion encountered during the fractionation, their order is in the direction predicted by the model equations.   The Schlieren patterns obtained by ultracentrifugation did not show a bimodal distribution for the incremental polymers; however, the difference in molecular weights of the peaks is probably too small for resolution by the instrument employed.   The Schlieren patterns did show a slightly narrower distribution for the incremental polymer.

Efficiency of modification by use of the incremental addition of *tert*-nonyl mercaptan is notable.   This is especially evident when a comparison is made with the control procedure using *tert*-dodecyl mercaptan (Tables I and II).   Significantly, the saving can be accomplished with no apparent sacrifice in raw polymer or vulcanizate properties.

Studies are in progress to determine the parameters of mercaptans necessary for accomplishing effects predicted by model equations for both emulsion and solution polymerization systems.   Simulated calculations with the model equation derived for incremental addition of modifiers to solution systems also give a minimum for a $\bar{P}_v$ versus conversion of increment plot.

CONCLUSIONS

Significant differences in modification can be realized by incremental addition of certain mercaptans in emulsion free-radical systems for polymerization of butadiene–styrene mixtures if the following conditions are fulfilled.

(*1*)   The additions of the increments of mercaptan should be so scheduled that gel is not formed during the interval of additions.

(*2*)   The molecular weight or solubility of the mercaptan should be such that under the conditions of the experiment a distribution of the modifier between phases is attainable in a reasonably short time.

(*3*)   An optimum set of conditions for certain mercaptans, such as *tert*-nonyl mercaptan, exists so that the greatest efficiency in utilization of these mercaptans by incremental addition is attainable.

(*4*)   When the proper conditions are fulfilled, incremental addition of certain mercaptans to 5°C.   SBR emulsion polymerization systems can result in uniform polymer viscosities during polymerizations, change in

molecular weight distribution, and more efficient utilization of mercaptan without apparent sacrifice of raw or vulcanizate properties in the ASTM standard formulations.

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Résumé

Une équation-modèle, déduite pour relier le degré moyen de polymérisation viscosimétrique $(\bar{P}_v)$ à l'addition progressive de modificateurs: $\bar{P}_v = K\{(\exp\{arx_1\} - 1) + [2/(2 + \exp\{x_1r\})]^a(\exp\{arx_2\} - \exp\{arx_1\})\}^{1/a}$ indique qu'un minimum dans la courbe $\bar{P}_v$/conversion devrait avoir lieu par addition d'incréments x_1. L'addition de mercaptan t-dodécylique à des échantillons de SBR à 5°C, montre des effets contraires à ceux prédits par l'équation-modèle mais l'addition par incréments de mercaptans t-nonyliques provoque un minimum dans les courbes viscosité/x_1, modifie la distribution des poids moléculaires et requiert 34% de poids en moins en mercaptan que n'exigerait le mercaptan t-dodécylique (tout le mercaptan t-C_{12} ajouté initialement). L'addition par incréments de mercaptan t-nonylique dans des réacteurs autoclave pilotes de 20 gallons, donne essentiellement les mêmes résultats que ceux trouvés au laboratoire sur plus petite échelle. Les propriétés de tension-élongation et de mélange du polymère, modifié par incréments et le contrôle modifié par mercaptan t-dodécylique, étaient essentiellement les mêmes aux erreurs expérimentales près. On donne les conditions requises pour la réussite des applications de la technique par modificateur additionné par incréments.

Zusammenfassung

Eine für den Viskositätsmittelwert des Polymerisationsgrades $(\bar{P}_v)$ beim Zusatz von Reglerinkrementen abgeleitete Modellgleichung, $\bar{P}_v = K\{(\exp\{arx_1\} - 1) + [2/(2 +$

$\exp\{x_1r\}$)]^a($\exp\{arx_2\}$ − $\exp\{arx_1\}$)]}$^{1/a}$, zeigt, dass in einer Kurve $\bar{P}_v$ gegen den Umsatz, bei welchem die Inkremente zugeführt werden, ein Minimum auftreten sollte, x_1. Der Zusatz von Inkrementen des handelsüblichen t-Dodecylmercaptans zu SBR-Rezepten bei 5°C zeigte einen zu dem von der Modellgleichung verlangten entgegengesetzten Einfluss, Versuche mit Zusatz von t-Nonylmercaptaninkrementen führten jedoch zu einem Minimum in der Kurve Viskosität gegen x_1, änderten die Molekulargewichtsverteilung und erforderten 34 Gewichts-% weniger Mercaptan als die t-Dodecylmercaptan-Kontrollversuche (das gesamte t-C_{12}-Mercaptan am Anfang zugesetzt). Zusatz von t-Nonylmercaptaninkrementen im Technikums-20-Gal.-Autoklavenreaktor lieferte im wesentlichen die gleichen Ergebnisse wie die Laboratoriumsversuche. Die Spannungs-Dehnungsund Mischungseigenschaften des durch Inkrementzusatz modifizierten Polymeren und des t-dodecylmercaptanmodifizierten Kontrollpolymeren waren innerhalb der Versuchsfehler im wesentlichen gleich. Bedingungen für die erfolgreiche Anwendung des Reglerinkrementverfahrens werden angegeben.

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