oxygenation of a conjugated diene, solanone, was found by Johnson and Nicholson (1965) to yield norsolanone. In a separate experiment compound IX was readily converted to XI by UV photolysis. Compound X was found to form readily under these conditions.

The compounds synthesized in these studies showed an important finding concerning the dehydration of α-ionol. Isomerization of IX to form several double-bond isomers analogous to megastigmatrienones (Figure 1) was not found in this study. The formation of X most likely involved a carbonium ion intermediate derived from megastigmatriene. Presently, we are examining other related systems to determine the exact mechanism.

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Statistical Evaluation of Thermally Modified Sulfur as a Coating Agent for Urea Granules

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The recently developed technology of using sulfur as an effective coating material for fertilizers to provide controlled release of the plant nutrients represents a potentially large-scale commercial use of the element. Because sulfur is needed in only small amounts as a plant nutrient, ways to reduce the total coating weight in production of slow-release fertilizers are of interest. This report evaluates the effect of heat treatment as a method to modify the properties of commercial-grade sulfur. Particular interest is focused on how these thermally induced changes in the sulfur may affect the dissolution rates of sulfur-coated urea (SCU) granules.

The National Fertilizer Development Center, Tennessee Valley Authority, Muscle Shoals, AL, has for several years been developing controlled-release fertilizers by coating water-soluble substrates with multiple layers of sulfur. Most of this work has been concentrated on the sulfur-coated urea (SCU) process (Young, 1974). Numerous greenhouse and field tests have shown this material to be a superior source of nitrogen for certain row crops and turf grasses. This product also has some physical advantages over conventional fertilizers in handling and resistance to caking under humid conditions. However, the cost of the sulfur application and the diluting effect the extra sulfur has on the overall nutrient value of the product must be considered its main disadvantages. Means to reduce the sulfur requirements to give a product with desirable release characteristics would therefore be of interest.

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Experiments have shown that nitrogen is released rapidly from individual granules once the coating fails and water gets access to the substrate. Therefore, it seems likely that it should be possible to control the N release not only by the thickness of the sulfur coat but also to some degree by improvement of the mechanical strength of the sulfur. The data presented in this paper show that when commercial-grade sulfur is heated above 200 °C, a redistribution of the sulfur allotropes occurs and that a significantly higher portion of these allotropes remains in the polymeric state when the sulfur is cooled to room temperature. Earlier work (Dale and Ludwig, 1965) has shown that a high level of polymeric sulfur increased the tensile strength of sulfur. The data from this study show how such thermally induced changes in the properties of sulfur will affect the release of nitrogen from urea granules coated with this modified sulfur.

EXPERIMENTAL SECTION

The sulfur used in these experiments was commercial grade, dark colored, Frasch-process sulfur supplied to us by Texasgulf, Inc. Organic carbon represents the major impurity in Frasch sulfur, ranging in concentration from

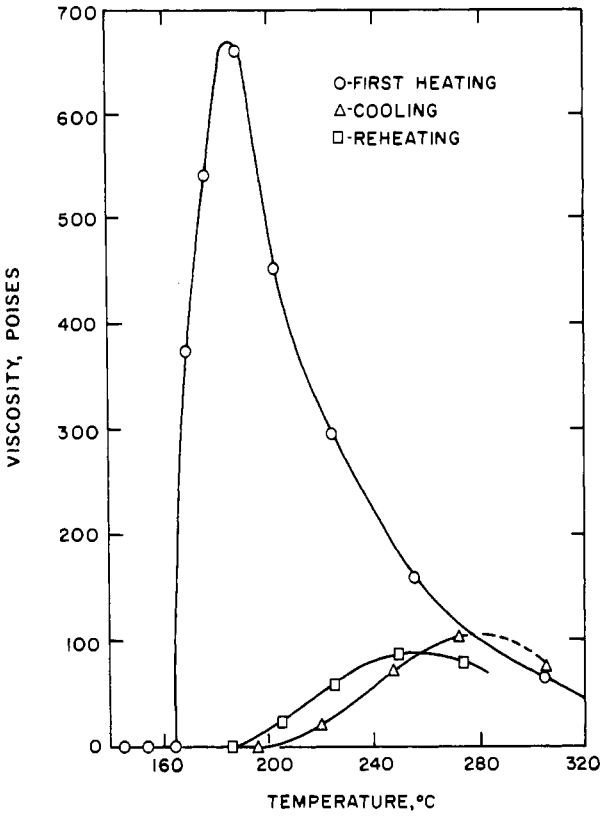

Figure 1. Effect of heat treatment on viscosity of unrefined, Frasch-process sulfur melts.

about 2000 to 5000 ppm (Meyer, 1965). The urea used was unconditioned granules (96%, −6 + 10 mesh) supplied by the Cominco Corporation of Canada. Viscosity measurements were done with a modified Ostwald viscometer of similar design to that used by Bacon and Fanelli (1943).

The amount of polymeric sulfur (S_π) was determined by carbon disulfide extractions using 10 mL of CS_2 for every g of sulfur. The samples were extracted for 10 min and filtered on a medium-coarse glass frit. The urea granules were coated by a small-scale version of the TVA "falling curtain type" sulfur-coating urea plant, which has been described elsewhere (Shirley and Meline, 1975). The coating experiments were designed to reveal statistical information on the effect of four independent process variables on the dissolution rates of the SCU products. These variables were temperature of the sulfur melt, T_s, temperature of the urea substrate, T_u, temperature of heat treatment, T_t, and weight percent of sulfur coating, WS. Dissolution rates were determined by submerging 50-g portions of the SCU products in 250 mL of water and measuring the amount of urea in solution after 3, 7, 14, and 28 days. The samples were kept in a thermostated oven set at 37.8 °C for the period of time indicated. For operating conditions and dissolution rate data, see paragraph at end of paper in regard to supplementary material available.

MODIFICATION OF SULFUR BY THERMAL TREATMENT

The physical properties of sulfur depend on such factors as the purity, previous temperature history, and relative concentration of sulfur allotropes. Bacon and Fanelli (1943) found that preheating a sample of sulfur containing 0.038% oil and 0.05% H_2SO_4 to temperatures above 200 °C reduced the maximum viscosity from about 560 P to less than 40 P. We have measured the viscosity of unrefined Frasch-process sulfur by using the method of Bacon and Fanelli and found that the organic carbon naturally present in this commercial-grade sulfur does indeed affect the properties of the sulfur that are subjected to thermal treatment. The results of these viscosity measurements are presented in Figure 1. The sulfur melt in these experiments was heated and cooled at about 0.5 °C/min.

Table I. Effect of Temperature on Properties of Unrefined, Frasch-Process Sulfur

temp, °C	η (viscosity), cP	S_π fraction insol in CS_2, wt %	W (chain concn), mol/kg	P (chain length), in S_8 units
		First Heating		
140	11.5	0.43	0.0168	37.7
150	11.1	0.96	0.0374	21.6
160	11.4	2.3	0.0897	14.8
170	38600	6.4	0.250	90820
180	60300	12.4	0.48	85980
190	64500	18.2	0.71	69100
200	48000	22.1	0.86	49730
210	39800	25.1	0.98	42450
220	33400	27.4	1.07	38790
230	28400	29.1	1.13	36350
240	22400	30.6	1.19	32150
250	18200	31.9	1.24	29970
260	15300	32.8	1.28	29070
270	13200	33.4	1.30	30400
280	11100	33.6	1.31	
290	9500			
300	7900			
		Reheating		
150	11	5.5	0.21	3.1
160	11	12.0	0.47	2.2
170	30	18.3	0.71	9.0
180	100	21.8	0.85	38.3
190	800	23.8	0.93	424
200	2000	24.9	0.97	1321
210	3400	25.4	0.99	2823
220	5100	25.6	1.00	5297
230	6750	25.5	0.99	8646
240	7800	25.4	0.99	12320
250	8300	25.3	0.99	16150
260	7980	25.2	0.98	18970
270	7250	25.0	0.98	21650
280	6000			

According to generally accepted theory, the rather abnormal viscosity behavior of sulfur melts heated above the transition temperature (159 °C) can be explained by the formation of long-chain polymeric sulfur molecules. Apparently heat treatment inhibits the growth of extremely long chains, which causes the high viscosity values of untreated sulfur at temperatures above 159 °C. The number-average chain length, P, of sulfur polymers may be derived from determination of the chain concentration, W, and viscosity measurements by applying the general theory of the viscosity–chain length relationship that has been worked out for high polymer solutions (Scott et al., 1949). Touro and Wiewiorowski (1966) considered the sulfur polymers as a pseudosolute dissolved in a pseudosolvent consisting of S_8 ring sulfur and used the following formula to calculate the average chain length:

$$P = [(\eta - \eta_o)/(\eta_o W)]^{1.1} \quad (1)$$

In this formula η is the viscosity of the sulfur melt, η_o is the viscosity of the pseudosolvent, and W is the concentration of sulfur polymers.

Applying eq 1 to our data, we obtained the results presented in Table I. The chain concentration, W, used in these calculations was determined from CS_2 extractions of quenched sulfur melts, and η_o was read from the data of Touro and Wiewiorowski (1966).

Table II. Levels of Variables Used in Coating Experiments[a]

process variable T_s, °C	coded variable X_1	process variable T_u, °C	coded variable X_2	process variable T_t, °C	coded variable X_3	process variable WS, % S	coded variable X_4
137.78	−2	62.78	−2	154.44	−2	22	−2
143.33	−1	68.33	−1	182.22	−1	24	−1
148.89	0	73.89	0	210.0	0	26	0
154.44	1	79.44	1	237.78	1	28	1
160.00	2	85.00	2	265.56	2	30	2
165.56	3	90.56	3		3	32	3

[a] Relationship between process and coded variables: $T_s = 148.89 + 5.56(X_1)$; $T_u = 73.89 + 5.56(X_2)$; $T_t = 210.0 + 27.78(X_3)$; WS = $26 + 2(X_4)$.

It is notable that the viscosity of the heat-treated sulfur at temperatures below 160 °C is not significantly different from that of untreated sulfur. Apparently the effect of the higher chain concentration in the heat-treated sulfur is offset by a significant reduction of the number-average chain length. Low viscosity values in the critical temperature range between 140 and 160 °C are considered important for good spray application of the sulfur.

EFFECT OF HEAT TREATMENT ON THE RELEASE OF UREA FROM SULFUR-COATED GRANULES

Due to the many variables that may affect the quality of SCU granules, it was considered necessary to obtain dissolution data from a relatively large number of runs and treat the data statistically. Spraying tests of a central composite design (Cochran and Cox, 1957) were carried out by using bench-scale sulfur-coating equipment (Shirley and Meline, 1975).

The results of dissolution rate measurements were fitted to a multiple quadratic regression equation of the form

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{14}X_1X_4 + B_{23}X_2X_3 + B_{24}X_2X_4 + B_{34}X_3X_4 + B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2 + B_{44}X_4^2 \quad (2)$$

In this equation, the dependent variable Y represents dissolution rates of the products and the independent variables X_1, X_2, X_3, and X_4 are the coded values of T_s, T_u, T_t, and WS, respectively. The levels of variables used in these experiments are presented in Table II. The results of variance analysis are presented in Table III.

The data show that all four process variables are highly sigificant factors in controlling the dissolution rates of the SCU products. About 90% of the variation in Y can be explained by variations in these four variables. The effect of the coating weight is the most significant source of variation, as was expected. It is surprising that the effect of the heat treatment on the 3- and 7-day dissolution rate data is the second most important factor. This effect decreases with increasing dissolution time. However, this may be a desirable feature of the heat treatment since an initial slow release of urea from the coated granules increasing with time is a desirable release pattern.

The dissolution rates of the SCU granules were found to decrease with increasing values of the urea substrate temperature within the testing range of 63–90 °C. Variations in the sulfur melt temperature do not affect the dissolution rates nearly as much as comparable variations in the urea temperature.

A minimum in the 7-day dissolution rate response surface was found to occur for a T_s value of about 148 °C. Using the values of the regression coefficients presented in Table III, we calculated contour lines of constant dissolution rates from the regression equation and the results are shown in Figure 2. These lines represent the 7-day dissolution rate response surface to variations in T_u and T_t for a typical product prepared with a sulfur melt temperature of 149 °C and having 26% sulfur coating.

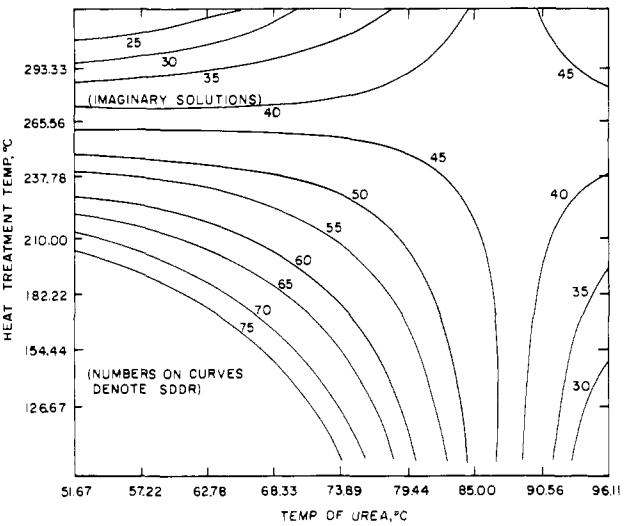

Figure 2. Effect of heat treatment of urea temperature on 7-day dissolution rate (SDDR). Sulfur weight = 26%; temperature of sulfur = 149 °C.

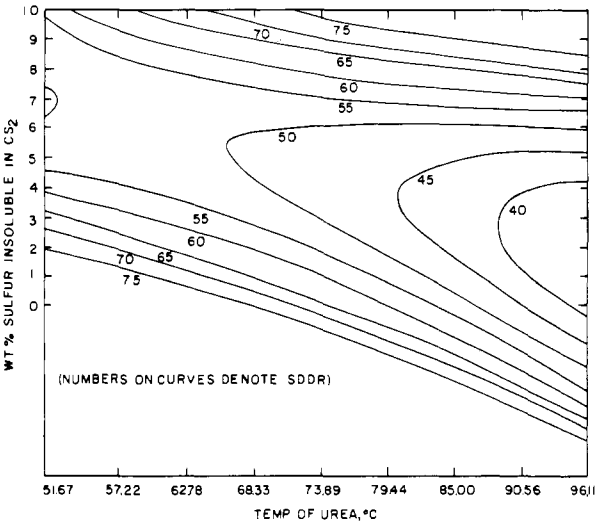

Figure 3. Effect of polymeric sulfur content and urea temperature on 7-day dissolution rate (SDDR). Sulfur weight = 26%; temperature of sulfur = 149 °C.

Dale and Ludwig (1965) have shown that the mechanical properties of sulfur may be related to the proportion of sulfur in the polymeric form (S_n). The effect of S_n as an independent source of variation in Y was determined by using the polymeric sulfur content as a variable in the regression analysis. Using data from only one level of heat treatment (238 °C) with S_n substituting for the heat treatment variable, we obtained the results as presented in Table IV. The polymeric sulfur content is apparently a highly significant factor in controlling the dissolution

Table III. Regression Analysis of Experimental Data for Heat-Treated Sulfur

source	regression coeff, B values	SE of B values	F values
	3 Days		
B_0	41.94		
X_4	−8.13	0.31	708.2[a]
X_2	−3.70	0.42	79.1[a]
$X_1 \cdot X_1$	1.80	0.24	56.7[a]
X_3	−5.54	0.51	115.7[a]
$X_4 \cdot X_4$	0.43	0.09	25.3[a]
X_1	1.08	0.33	10.8[a]
$X_2 \cdot X_3$	1.62	0.40	16.5[a]
$X_3 \cdot X_4$	0.92	0.28	11.1[a]
$X_1 \cdot X_4$	0.47	0.16	9.1[a]
$X_2 \cdot X_4$	0.32	0.16	4.0[b]
	SE in $Y = 7.1$; $R = 0.908$		
	7 Days		
B_0	52.97		
X_4	−8.21	0.25	1088.0[a]
X_2	−4.13	0.47	76.8[a]
$X_1 \cdot X_4$	0.69	0.18	14.8[a]
X_3	−5.21	0.53	95.6[a]
$X_1 \cdot X_1$	1.79	0.27	42.5[a]
$X_2 \cdot X_3$	2.15	0.42	25.9[a]
$X_4 \cdot X_4$	0.42	0.10	18.6[a]
X_1	1.12	0.38	8.7[a]
	SE in $Y = 8.2$; $R = 0.902$		
	14 Days		
B_0	61.55		
X_4	−7.93	0.26	896.9[a]
$X_1 \cdot X_4$	0.79	0.19	17.3[a]
X_2	−4.03	0.51	61.1[a]
X_3	−3.66	0.70	27.4[a]
$X_1 \cdot X_1$	1.51	0.29	27.0[a]
$X_2 \cdot X_3$	2.40	0.50	22.9[a]
$X_4 \cdot X_4$	0.29	0.10	7.6[a]
$X_3 \cdot X_3$	−1.61	0.65	6.1[b]
X_1	0.74	0.41	3.2[c]
	SE in $Y = 8.7$; $R = 0.886$		
	28 Days		
B_0	69.46		
X_4	−7.44	0.25	879.1[a]
$X_1 \cdot X_4$	0.87	0.20	19.2[a]
X_2	−3.64	0.54	44.9[a]
$X_3 \cdot X_3$	−2.39	0.67	12.8[a]
$X_2 \cdot X_3$	2.14	0.53	16.4
$X_1 \cdot X_1$	1.10	0.31	12.5[a]
X_3	−2.73	0.73	14.0[a]
$X_1 \cdot X_2$	0.55	0.33	2.8[c]
	SE in $Y = 9.2$; $R = 0.869$		

[a] Significant at 99% or greater confidence. [b] Significant at 95% or greater confidence. [c] Significant at 90% or greater confidence.

rates of SCU granules. The optimum range of this variable can be estimated from the contour curves presented in Figure 3. It is seen that low dissolution rates are favored by high substrate temperature (a practical upper limit is about 91 °C) and a polymeric sulfur content around 3%.

Table IV. Regression Analysis of 7-Day Dissolution Rate Data with S_n as a Variable

source	regression coeff, B values	SE of B values	F values
B_0	67.48		
X_4	−8.30	0.30	869.4[a]
$X_3 \cdot X_3$	1.00	0.13	140.9[a]
X_3	−8.80	1.64	21.4[a]
$X_4 \cdot X_4$	0.40	0.10	16.4
X_2	−7.28	1.27	9.2[a]
$X_2 \cdot X_3$	1.22	0.24	20.8[a]
$X_1 \cdot X_3$	−0.37	0.16	5.1[b]
	SE in $Y = 7.4$; $R = 0.922$		

[a] Significant at 99% or greater confidence. [b] Significant at 95% or greater confidence.

Somewhat higher S_n values are desirable in products which are prepared at lower substrate temperatures. Minimum values of the dissolution rates for any combinations of T_u and S_n can easily be read from the contour lines in Figure 2.

The results of these tests show that heating commercial-grade sulfur to temperatures above 200 °C before it is cooled down to a temperature range where spraying is possible may be a practical way to improve the properties of sulfur as a coating agent for urea granules.

The data show significantly reduced dissolution rates from urea granules sprayed with this thermally modified sulfur. Apparently the high level of S_n in this sulfur improves its mechanical strength. Less sulfur should, therefore, be needed to produce a product with desirable release characteristics. However, since the data presented in this paper were based on small-scale equipment, confirmation of the data from test spraying on a larger scale would be highly desirable.

Supplementary Material Available: Operating conditions and dissolution rate data for SCU granules (5 pages). Ordering information is given on any current masthead page.

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