to be derived from slow release may not be regarded as completely lost. The unsolubilized glass remaining in the soil will continue to release boron slowly for crops of subsequent seasons. On the basis of these considerations, the most suitable mill products were the 2-hour grind of 176-C, and the 0.5-hour grinds of 176-E and -F. The average effectiveness of these materials relative to borax was 0.6 ± 0.1 in the first two harvests. Over-all performance of such glass carriers can be improved greatly by narrowing the particle size range.

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FERTILIZER CONTAMINANTS

Rate of Biuret Formation from Urea

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To determine the amount of biuret formed under conditions encountered in the manufacture and transportation of urea, a kinetic study of the available data has been made. The rate constants of biuret formation from urea at different temperatures were determined and the results of calculations on biuret formation in urea solutions under various conditions are presented.

One of the main by-products obtained on heating urea, either in solid form or in aqueous solution, is biuret. However, the exact mechanism of biuret formation is not fully known and the literature on the kinetics of biuret formation is extremely limited (*1–7*).

A considerable amount of urea is used as fertilizer, in which the presence of biuret has to be controlled, because of its detrimental action on plants and leaves. It is therefore desirable to be able to estimate the rate of biuret formation from urea under various conditions. The results of a kinetic study, utilizing available data in biuret formation from urea are presented here. A weighed urea solution was heated at the desired temperature in a sealed glass test tube without stirring. It is believed that the data are valid for the usual conditions encountered in the production and transportation of urea.

Kinetic Study

At high temperatures, urea undergoes complex reactions to produce a mixture of several compounds, including triuret and cyanuric acid. However, under usual plant operating conditions for producing urea, the extent of formation of such compounds is relatively insignificant, as compared to the amount of biuret formation. Moreover, at the temperatures generally encountered in the transportation of urea, the formation of such compounds as well as the dissociation of urea into ammonia and carbon dioxide is relatively insignificant.

Therefore, the rate constants presented herein have been developed without consideration of the amounts of substances formed other than biuret as shown by the following equation:

$$2NH_2—CO—NH_2 \rightarrow NH_3 + NH_2—CO—NH—CO—NH_2$$

Then

$$\frac{d}{dt}(NH_2—CO—NH—CO—NH_2) = \frac{d}{dt}(NH_3) = \frac{-d}{dt}(NH_2—CO—NH_2)^2$$

$$\frac{dx}{dt} = k(a-x)^2 \quad (1)$$

where

d/dt = change of concentration with respect to time
a = initial concentration of urea in the solution, moles per liter
x = number of moles of urea reacted in the interval time t
t = time in hours
k = rate constant of the formation of biuret

$$\frac{dx}{(a-x)^2} = kdt \quad (2)$$

$$\frac{1}{a-x} = kt + c \quad (3)$$

when $t = 0$, $x = 0$. Hence

$$c = \frac{1}{a} \quad (4)$$

Substituting Equation 4 into 3,

$$kt = \frac{x}{a(a-x)} \quad (5)$$

Assuming $P = \frac{x}{a}$, the fraction of urea converted to biuret, is then

$$kt = \frac{P}{a(1-P)} \quad (6)$$

These kinetic equations were applied to the available data (*5*). The rate constant of the reaction at 140° C. was calculated and the results are shown in Table I, which verifies the validity of the treatment because the rate constant remains substantially the same. The rate constants at different temperatures were determined in a similar manner and are reported in Table II.

Activation Energy

From Table II, when the logarithm of the rate constant is plotted against the reciprocal temperature (1/°K.), it is possible, by the Arrhenius equation, to obtain the energy of activation of biuret formation from urea at the temperature range of 50° to 170° C. Such an Arrhenius plot gives an essentially straight line, from which the activation energy is estimated as 20.3 kcal. per mole. By use of such rate constants the rate of biuret formation in urea solutions at different concentrations can be calculated for any temperature. Although biuret is formed at almost constant rate even at high temperatures, a progressive decrease occurs with time at the high temperature levels due to the slow condensation of biuret to triuret. However, the decrease is so slight that for practical purposes, it can be ignored. Thus,

Table I. Formation of Biuret from Dry Urea at 140° C.

Time, Hours	Urea Converted to Biuret, P	Rate Constant, k, Liter/Mole Hr.
0.25	0.010	1.9×10^{-3}
0.5	0.022	2.1×10^{-3}
0.75	0.028	1.8×10^{-3}
1	0.035	1.7×10^{-3}
2	0.061	1.5×10^{-3}
4	0.122	1.61×10^{-3}
5	0.150	1.63×10^{-3}
6	0.155	1.41×10^{-3}
7	0.195	1.60×10^{-3}
	Average	$(1.68 \times 0.15) \times 10^{-3}$

Table II. Rate Constant of Biuret Formation from Urea

Temp., ° C.	Rate Constant, k, Liter/Mole Hr.
50	3.98×10^{-6}
80	2.38×10^{-5}
100	6.55×10^{-5}
140	1.68×10^{-3}
150	3.34×10^{-3}
160	5.66×10^{-3}
170	8.28×10^{-3}

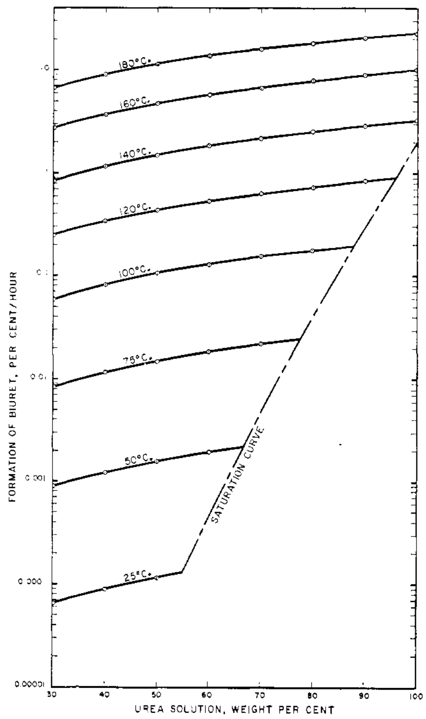

Figure 1. Rate of biuret formation in urea solution

the rates of biuret formation for the conditions shown in Figure 1 are presented on an hourly basis.

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INSECT REPELLENT TOXICITY TO ANIMALS

The Toxicology of Butoxypolypropylene Glycol 800 (Crag Fly Repellent)

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This study was undertaken to characterize the toxicity of butoxypolypropylene glycol 800 (BPG 800) by single and repeated doses to rodents and dogs, so that its acceptability for use as a fly repellent could be ascertained. Single-dose studies show that BPG 800 has only slight oral and skin penetration toxicity for rodents and does not increase toxicity when fed orally to rats with nine available insecticides. Subcutaneous and intraperitoneal injection, compared with direct intravenous injection, demonstrates that BPG 800 passes tissue barriers poorly and offers little or no hazard by the usual portals of entry to the body. It is not stored in the bodies of animals, and 50% or more of a single dose may be found in the urine unchanged. Rats tolerated 640 p.p.m. in the daily diet in chronic feeding for 2 years, while dogs tolerated 890 p.p.m. for 1 year.

The acute and subacute toxicity studies completed prior to 1951 by Carpenter and associates (*1*) elucidated the suitability and safety of butoxypolypropylene glycols (BPG) 400 and 800 as fly repellents. This publication covered all portals of entry, as well as irritation tests and studies on absorption and excretion in rats. Granett *et al.* (*3*, *4*) demonstrated the effectiveness of formulated BPG 800 as a fly repellent for livestock and in particular for dairy cattle. This compound and other members of the same series have wide solvent properties; some find use as specialty lubricants and as hydraulic fluids. Increasing uses have led to the more extensive toxicological study now reported.

BPG 800, sold as Crag Fly Repellent (Union Carbide Corp.), has a specific gravity of 0.990 and a water solubility of 0.1% at 20° C. The compound is a clear liquid, substantially nonvolatile, with a vapor pressure under 0.1 mm. of mercury at 20° C. It is soluble in most organic solvents, including alcohols, ketones, toluene, and gasoline, and is miscible with the ingredients most useful in the formulation of insecticides such as petroleum distillate and methylated naphthalene.

The present paper brings up to date the information which has been developed on acute toxicity orally, by skin penetration, and by injection of BPG into four rodent species during the period