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METHOD OF PRODUCING PHOSPHORUS PENTASULFIDE OF CONTROLLED REACTIVITY

Stephen Robota, North Tonawanda, N.Y., assignor to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

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This invention relates to a process for the preparation of phosphorus pentasulfide. More specifically this invention resides in the preparation of phosphorus pentasulfide of controlled reactivity.

In the production of phosphorus pentasulfide (P_4S_{10}) the heretofore known processes resulted in a product of chance reactivity. P_4S_{10} is manufactured commercially by reacting liquid phosphorus and sulfur in approximately stoichiometric proportions. The final step in a typical process consists of pouring molten P_4S_{10} into molds, drums or other containers for solidification. This solidification occurs at a slow rate, necessitating a cooling period of up to forty-eight hours depending upon the size of the mold. The rate of cooling under such conditions is non-controllable. The resulting product is one of varied reactivity, the P_4S_{10} on the outer periphery having a different rate of reactivity than the product of the inner portion of the mold. The problem faced by those in the art, therefore, has been to develop a method to make a P_4S_{10} product of reactivity controllable to suit the needs of the individual users. It has been found that a definite relationship exists between the cooling rate through the liquid-solid transition zone to the reactivity of the product obtained. Rates of cooling below the transition zone have an effect on reactivity but not as substantial an effect as do the rates through the liquid-solid transition zone. The present methods of mold filling do not permit any control of reactivity since mold cooling in general is uncontrolled. In the event that a customer wanted a P_4S_{10} of a given reactivity, the best that could be done was to determine the reactivities of the already produced P_4S_{10}, and send to the customer the product closest meeting these requirements. This was an undesirable system both from the producer's and the buyer's view point. It necessitated a large produced stock on hand and a further time consuming step of analyzing for reactivity. In the process of this invention a P_4S_{10} product of desired reactivity can be supplied to the buyer from the production line. No huge stock pile of product of assorted reactivities need be kept. The inventive concept of this invention is the correlation between reactivity and the rate of P_4S_{10} cooling through the range of 280 to 260 degrees centigrade. It has been found that the cooling rate through the phase transition is the most important factor in controlling reactivity. It should be mentioned that P_4S_{10} manufactured by any method may utilize the teachings of this invention. Variations in the rate of cooling outside the phase transition range have relatively less, although some, effect on reactivity. This finding represents a valuable contribution to the art because it permits regulation of reactivity in a manner adaptable to continuous automatic processing, resulting in economics in equipment, storage space, labor and process materials.

A procedure used to determine the reactivity of a P_4S_{10} product is as follows:

EXAMPLE 1

Four hundred milliliters of anhydrous ethanol (other

alcohols can be used, for example cyclohexanol) were added to a dry, three-necked Dewar flask. In the three openings or necks of the Dewar were inserted a stopper, a thermometer and a stirrer. The stopper was removed and an immersion heater was placed in the Dewar. The heater can be used with a 110 volt line. It was sometimes necessary to stop the heater for short periods in order to prevent local boiling of the alcohol. When the temperature reached 51 to 52 degrees centigrade, the heater was removed and the small stopper was replaced in the opening. The flask was then allowed to reach a steady-state condition. During the initial ten minutes there was a moderate decrease in the temperature of the apparatus, and the temperature drop became constant at about 0.075 degree centigrade per minute. Although this temperature drop sometimes varies because of the differences of room temperature, it should never exceed 0.1 degree centigrade per minute. While the apparatus was cooling to about 50 degrees centigrade, 60 grams of the sample phosphorus pentasulfide were weighed in a 150 milliliter beaker covered with aluminum foil. When the temperature of the Dewar reached exactly 50 degrees centigrade, the small stopper was removed and a powder funnel was inserted therein. The stopwatch was started at the same time as the addition of the sample to the apparatus was begun. The time required for addition of the sample was 15 to 30 seconds. After the sample was added, the powder funnel was removed and the small stopper was replaced. The temperature of the apparatus was recorded at intervals of 0.5, 1.0, 2.5 minutes, 5 minutes, 10 minutes and 20 minutes, after the start of the addition of the sample. The amount of sample reacted at each time was calculated. The method of calculation is indicated below.

Calculations (for procedure using ethanol):

$$\text{Percent reacted} = \left[\frac{(216+cC.)(T-50+0.062t)=330)}{5280}\right]100$$

where

cC. is the calorimeter constant in cal. per degree centigrade. It is equal to 66 cal. per degrees centigrade for calorimeter #2.

t is the time in minutes after addition of sample.

T is the temperature in degrees centigrade at time, t.

216 is the heat capacity in cal. per degree centigrade of the reaction product.

0.062 is the cooling rate of the reaction product and calorimeter in degrees centigrade per minute.

330 is the correction in cal. due to the introduction of cold sample.

5280 is the heat of reaction in cal. under the conditions of the test.

For all P_4S_{10} cooling tests graphs were plotted representing the temperature decrease versus time relationship. From these curves the liquid solid phase transition rate was thus determinable and was henceforth correlated with the resultant reactivities (see table below) of the samples. The phase transition occurred within the range 280°–260° C. for all nominal compositions of P_4S_{10}. The effect of cooling after solidification was also investigated (for example beaker experiments tests) but effect found negligible.

The following example shows P_4S_{10} phase transition rate versus reactivity on P_4S_{10}.

EXAMPLE 2

Reactivity [1]	Time of cooling P_4S_{10} through phase transition range
10	2 minutes, 30 seconds.
11	1 minute, 48 seconds.
12	1 minute, 24 seconds.
13	1 minute, 6 seconds.
14	54 seconds.
15	42 seconds.
16	35 seconds.
17	30 seconds.
18	24 seconds.
19	20 seconds.
20	18 seconds.
50	1.2 seconds.
90	0.18 second.
100	0.125 second.

[1] Reactivity values refer to percent P_4S_{10} reacted with ethanol in 1 minute.

Various methods of cooling can be used by those employing process of this invention. Some of the cooling methods that may be suggested are belt-type cooler methods and flaker methods. Any method of cooling, however, which accomplishes the phase transition cooling of this invention is meant to be encompassed by this disclosure.

The following example further illustrates the method of this invention.

EXAMPLE 3

P_4S_{10} was fed on the roll of a flaker 12 inches in diameter and 18 inches long. The molten P_4S_{10} was maintained at 325 degrees centigrade, the roll was maintained at about 20 degrees centigrade while the flaked P_4S_{10} was at 66 to 84 degrees centigrade. The water feed rate to the roll was 100 to 112 pounds per minute. The roll speed was 7 to 10 revolutions per minute, thus giving a phase transition time (275 to 265 degrees centigrade) of 0.125 second. The flaking rate was 155 to 231 pounds per hour. The flake thickness measured 0.024 inch. The ground flake reacted 100 percent in one minute while the comparable average reactivity on the same batch of P_4S_{10}, but slow cooled in a cone, showed only 10 to 12 percent reacted with ethanol in one minute.

EXAMPLE 4

Pan Casting Cooling Tests

Molten plant prepared P_4S_{10} was fed directly on an 18 x 12 x 2 in. cast iron shallow pan. Along the bottom of this pan a thermocouple was extended and connected to a temperature recorder. Soon as the desired cake thickness was cast, the pan was covered and the temperature decrease versus time recorded. Five different cake thicknesses were prepared ranging from 0.55 in. to 0.119 in. The phase transition rates were 2.5 mins. for the former and 0.3 min. for the latter. The corresponding reactivities were 10.2 to 17.4 respectively. The other cake thicknesses had intermediary values, but holding to the relationship established for rate of phase transition versus reactivity.

EXAMPLE 5

Test Tube Cooling Experiments

Solid P_4S_{10} remelted and then cooled at different rates through the phase transition zone, resulting in reactivities dependent on established phase transition reactivity relationship rule. The effect of changes in cooling rates after solidification showed these changes to be quite insignificant.

EXAMPLE 6

Beaker Experiments

Molten, plant prepared, P_4S_{10} was fed directly to a 400-ml. Pyrex beaker. After filling to approximately ½ full, the beaker was covered with aluminum foil and a thermometer was immediately inserted in the liquid P_4S_{10}.

The temperature fall versus time was subsequently recorded. The following cooling conditions were imposed on the P_4S_{10}.

Test:

1—Atmospheric cooling at 25° C.

2—Quenched in ice water.

3—Atmospheric cooling but cooling rate retarded as compared to 1 by having the beaker insulated.

4—Atmospheric cooling but at 240° C. ice water quenched.

5—Atmospheric cooling but at 265° C. (solidification just completed) ice water quenched.

Test 3 showed longest phase transition time 14.1 mins. and gave reactivity of 8.0. Test 2 had phase transition time of 1 minute and reactivity of 12.4. The other tests fall in intermediate range. The effect of changing the cooling rate after solidification (tests 4 and 5) was small.

These tests were often done using same P_4S_{10}.

The examples of the cooling apparatuses and other specifics given in the foregoing specification have been given for purposes of illustration and not limitation. Many other modifications and ramifications will naturally suggest themselves to those skilled in the art, based on the disclosure of my basic discovery. These are intended to be comprehended within the scope of my invention.

I claim:

1. A process for controlling the reactivity of phosphorus pentasulfide which comprises controlling the cooling of molten phosphorus pentasulfide through the temperature range of from about two hundred eighty degrees centigrade to two hundred sixty degrees centigrade for a time interval between about 0.125 second and about 2.5 minutes.

2. A process for producing phosphorus pentasulfide of controlled reactivity which comprises reacting molten phosphorus with sulfur in approximately the stoichiometric proportions necessary to form phosphorus pentasulfide, and cooling the molten reaction mixture to yield solid phosphorus pentasulfide, said cooling step comprising a controlled cooling of the phosphorus pentasulfide reaction mixture through the liquid-solid phase transition range for a time interval between about 0.125 second and about 2.5 minutes.

3. A process for producing phosphorus pentasulfide of controlled reactivity which comprises reacting molten phosphorus and sulfur in approximately stoichiometric proportions necessary to form phosphorus pentasulfide, purifying the molten phosphorus pentasulfide reaction mixture, and cooling the molten phosphorus pentasulfide to yield solid phosphorus pentasulfide, said cooling step comprising a controlled cooling of the phosphorus pentasulfide through the liquid-solid phase transition range for a time interval between about 0.125 second and about 2.5 minutes.

4. A process for producing phosphorus pentasulfide of controlled reactivity which comprises reacting liquid phosphorus and sulfur in a reaction vessel in approximately stoichiometric proportions, distilling the reaction mixture to purify the phosphorus pentasulfide, and cooling the resulting molten phosphorus pentasulfide to yield solid phosphorus pentasulfide, said cooling step comprising a controlled cooling of the phosphorus pentasulfide through the liquid-solid phase transition range for a time interval between about 0.125 second and about 2.5 minutes.

5. A process for producing phosphorus pentasulfide of controlled reactivity which comprises reacting liquid phosphorus and sulfur in a reaction vessel in approximately stoichiometric proportions, distilling the reaction mixture to purify the phosphorus pentasulfide, and cooling the resulting molten phosphorus pentasulfide to yield solid phosphorus pentasulfide, said cooling step comprising a controlled cooling of the phosphorus pentasulfide from about

two hundred eighty degrees centigrade to two hundred sixty degrees centigrade for a time interval between about 0.125 second and about 2.5 minutes.

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