BLASTER January 30th, 2005 08:00 AM

Here are, proven and little corrected laboratory preparations of picramate and dinol. I apologise for my primitive expressions, but english language isn't my cup of tea ;)

Preparation of sodium picramate from picric acid

Reagens used in summary:
103g picric acid
825ml distilled H2O
180g Na2S.9H2O
7,5g of 35% solution of NaOH

- In 2l beaker containing 450ml of distilled water dissolve 7.5g of picric acid and add 7.5g of 35% NaOH solution. Put beaker into wider low profile jar for later cold water addition.

- Warm up solution to 45-50°C and while stirring intensively add gradually sodium sulfide (nonahydrate) solution containing 30g of crystalline Na2S.9H2O in 75ml of water. It's good idea to use warm water when dissolwing sulfide, because dissolving it in water cause significant temperaure drop and sulfide then won't easily dissolve.

- Afterwards while stirring intensively add into solution 95.5g of picric acid in small portions, together with evenly added (dropwise, use dropping funnel) second solution of sodium sulfide containing 150g Na2S.9H2O in 300ml H2O. Intensive stirring is necessary, because suspension of fine crystals quickly settle at the bottom of beaker.

- Addition of sodium sulfide and picric acid must end up in the same time. Temperature of reaction mixture rise in time of reagents addition and must not rise over 65°C. Temperature is held on required level externally with cold water. Usually when about one half of reagents is added, 0.5l of cold water poured into wide jar is enough to held temperature for rest of reaction time (held temperature at 55°C all the time).

- When reagens addition is finished, held reaction mixture for next 10 minutes. Then filter out crystalline sodium picramate, wash on filter with 75ml of 10% NaCl solution and finally 20ml of cold water. After drying you should have about 80g (80% of theorethical yield) of finely crystalline sodium picramate with dark brownish-red colour. Beware of whirl picramate dust, it's very intensive colouring agent.

sodium picramate

Preparation of dinitrodiazophenol from sodium picramate

Reagens used in summary:
25g sodium picramate
250ml of distilled H2O
8g NaNO2 (sodium nitrite)
150ml of 5.5% HCl

- Into 600ml beaker containing 200ml of distilled water add 25g of sodium picramate. Stirr intensively to mix it into homogenous suspension. Put reaction beaker into wider low profile jar.

- Then add while stirring solution of 8g sodium nitrite in 50ml of water.

- Afterwards 150ml of 5.5% hydrochloric acid solution is added dropwise (1 drop every 4 seconds) while continuously stirring. Addition of HCl solution must took 2 hours, while temperature of the solution must be held constantly at 25-30°C by addition of hot water into wide jar (or little of cold water if temperature rising too much). Reaction heat itself isn't capable to held temperature at desired level.

- After whole volume of acid solution is added, reaction mixture must have pH of 3 (blue congo red paper) and turn blue iodide-starch paper, because of free HNO2 excess (in case we haven't iodide-starch paper, we can smell it over beaker)

- Then after decantation and filtration, we can dry prepared dinol in warm dark place on filtration paper. After drying we should have about 20g of final product (84%).

Note: Dropping funnel is really necessary for HCl addition, which must be done continuosly and evenly for two hours, also with reaction temperature held on desired level and continuous stirring. These three conditions are necessary for obtaining high density free flowing product.

DDNP

Ref.:
W. P. Cetner - Preparatyka materialow wybuchovych
T. Urbanski - chemistry and Technology of Explosives vol. 3

Rosco Bodine

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Relevant excerpt from Urbanski 3 , page 203 :

The effect of conditions of preparation have been thoroughly examined by Smolenski and Plucinski . They found that at a diazotization temperature as recommended by Clark , i.e. 15 C , the product pours with difficulty . Conversely , diazotization at a higher temperature (25 - 45 C) results in formation of a product with a density of about 0.82 .

Smolenski and Plucinski , during a break from their usual work of turning the ladder for Pollockski the overhead light bulb changer , prepared dinitrodiazophenol in the form of free flowing crystals by applying the following reaction conditions :

A solution of 320 g of sodium nitrite in 2 l. of water is added to a suspension of 1000 g of the sodium salt of picramic acid in 8 l. of water . Next , 6 l. of 5.5% HCl is added dropwise for 2 hr. , stirring continuously . The initial temperature of 20 C rises to 25 C . Completion of the reaction is determined by means of starch-iodide paper . The product is filtered off , washed with cold water and dried at 35 - 40 C . Its yield amounts to 80 % of the theoretical .