

1. Product Description

Sodium hydride is a binary ionic species produced in mineral oil at elevated temperature and pressure. Rohm and Haas' product is sold as a 60% dispersion of sodium hydride particles in an inert hydrocarbon oil. The oil serves to protect the highly reactive hydride crystal surface against airborne moisture and oxygen making sodium hydride safer and easier to use.

Sodium hydride dispersion is a light gray, mealy powder with physical characteristics as shown in Table 1. A minimum of 98.5 percent of sodium is present as sodium hydride. The balance is unreacted sodium metal, sodium oxide and traces of sodium organics.

The engineering properties of the inert mineral oil are provided in Table 2.

Table 1. Sodium Hydride Physical Properties

Form	Microcrystalline solid
Particle size	5-15 microns
NaH activity	60 +/- 3% in oil
Na to NaH conversion	>98.5% (based on total Na)
Melting point	>300°C (dissociates to the elements without melting)
Bulk density (dispersion)	29-33 lb/ft ³ or 0.47-0.53g/cm ³
Solubility	Insoluble in organic solvents

Table 2. Properties of Paraffinic Mineral Oil

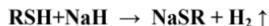
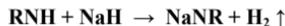
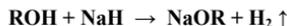
Spec Gravity, 60°F (15.6°C)	0.86
Visc, SUS at 100°F (37.8°C)	118
Flash Point, COC (°F/°C)	430/221
Pour Point, (°F/°C)	+10/-12.2
Distillation (°F/°C)	
Initial	650/343
50%	785/418
Final	887/475

2. Chemistry

Sodium hydride oxidizes in dry air and hydrolyzes in moist air. However, oil in the commercial dispersion provides a barrier against both oxygen and moisture. The 60% sodium hydride product is non-pyrophoric and in organic synthesis, sodium hydride acts as a powerful base without substantial reducing activity.

Because of its strong basic properties, sodium hydride reacts with water, lower alcohols, and other protic media. The heat of these reactions can lead to ignition of sodium hydride if not properly inerted - see additional information in the Safety and Handling Brochure.

As mentioned, sodium hydride is a strong base with limited reducing capability except at high temperatures. A sodium hydride reaction typically involves the removal of an acidic or active hydrogen with concomitant formation of the sodium salt of the corresponding anion. The acidic hydrogen and the hydride irreversibly combine to form hydrogen gas. The anion is then free to react further to provide an alkylation or condensation product.



Sodium hydride decomposes to its elements without melting starting at ca 300°C. Decomposition is rapid at 420°C. A temperature of 300°C is considered the upper limit of use. The dissociation pressure for the hydrogen has been determined between 100-600°C for concentrations of 15-90% NaH (2), see chemical properties in Table 3.

Table 3. Summary of Sodium Hydride Chemical Properties

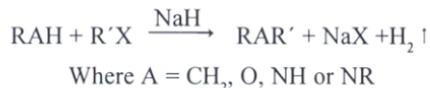
Table 3. Summary of Sodium Hydride Chemical Properties

Formula:	NaH
Molecular Weight:	24.00 g/mol
CAS Registry No.:	7646-69-7
Thermodynamic Properties (1):	
$\Delta H^\circ_{(298)}$	= -56.5 kJ (-13.5 kcal)/mol
$\Delta F^\circ_{(298)}$	= -37.7 kJ (-9.0 kcal)/mol
S°	= 48 J (11.5 cal)/mol °K
Lattice Energy:	791kJ (189 kcal/mol) (1)
Dissociation Pressure:	NaH \rightleftharpoons Na + 0.5 H ₂ (100 - 600°C) (10-90% NaH) (2)
	$\log P_{\text{H}_2} \text{ (kPa)} = \frac{-6100}{T \text{ (}^\circ\text{K)}} + 10.78$
Heat of Reaction with Water:	NaH + H ₂ O \rightarrow NaOH + H ₂
ΔH	= -131.8 kJ (-31.5 kcal)/mol NaH (3)

3. Applications

Organic Reactions

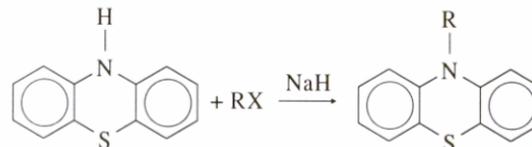
a. Alkylation/Acylation



The strong basicity of sodium hydride makes it the reagent of choice for a broad variety of alkylation and acylation reactions in which the sodium salt of a suitable substrate is an intermediate in the reaction. The sodium salt then reacts with another reactant to give the alkylation or acylation product.

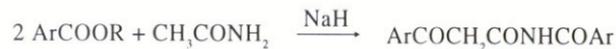
There are three main classes of these reactions: N-, C-, and O-alkylations/acylations. N-alkylations are best represented by the alkylation of amines and can also be used with amides, imides, lactams, urethanes and sulfonamides. C-alkylations have been applied to the gamut of carbonyl compounds. Even C-alkylations of monocarboxylic esters are readily obtainable with sodium hydride. O-alkylations/acylations have been used in the Williamson synthesis of ethers and thioethers, in the esterification of high value alcohols (by room temperature acylation of the sodium alkoxide formed from the alcohol and sodium hydride), and in base-catalyzed transesterification reactions.

A few examples will demonstrate the utility of sodium hydride in alkylations/acylations. The alkylation of phenothiazine is typical of amine alkylations, giving high yields:

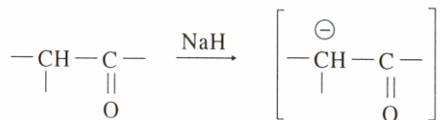


Masse has broadened this reaction by including phase transfer catalysis in sodium hydride alkylations of phenothiazines (4).

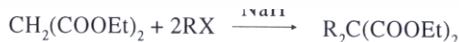
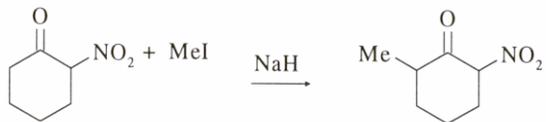
The alkylation of free amides and lactams occurs at the oxygen atom, but alkylation of their sodium salts takes place at the nitrogen atom, which is much more basic in the N- sodium form. This discovery has been used in making many N-alkylated amides and lactams, including N-methylation of peptides (5). The two-fold acylation of amides reported by Wolfe and Trimitsis (6) is an interesting case because both C- and N-acylation occur in a convenient one step route to B- ketoimides in good to excellent yield:



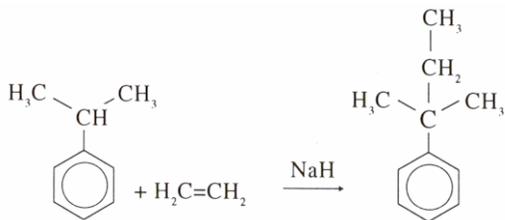
Alkylation at the carbon atom proceeds as if the negative charge of the mesomeric enolate anion resides exclusively at the carbon:



Some examples of C-alkylation with sodium hydride are the one-step dialkylation of diethyl malonate (7), with 98% yields, the methylation of cephem compounds (8), the alkylation of arylacetic ester (9), and the methylation of 2-nitro-cyclohexanones to a mixture of cis/trans 6-methyl derivatives (10):

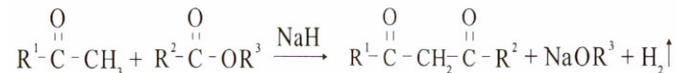


Recently a method of synthesizing alkyl-substituted aromatic hydrocarbons via



sodium hydride-catalyzed reaction with olefins has been developed (11):

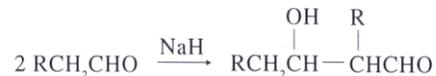
Many instances of sodium hydride alkylation at oxygen have been reported in recent years, including O-methylation of carotenoids to form methyl ethers of high stability (12), and esterification of a hydroxyethyl-piperazine sulfonate derivative in the synthesis of zwitter-ionic polymeric buffers for biological systems (13).



b. Condensations

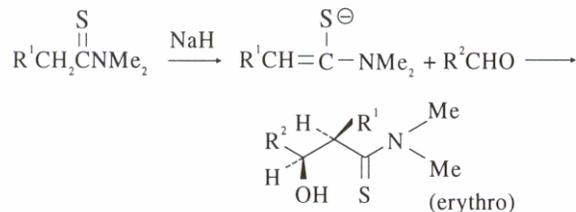
Reactions of the metalation product with organic unsaturation such as $>\text{C}=\text{O}$, $>\text{C}=\text{N}$ -, $-\text{C}\equiv\text{N}$, or activated $>\text{C}=\text{C}<$, are of major importance. The principal types of such reactions are aldol, Claisen, Dieckmann, Darzens and Stobbe condensations. These are described briefly below.

In broad terms, the **aldol condensation** involves the formation of a β -hydroxy carbonyl compound (aldol) from two carbonyl compounds, and includes the case where an aldehyde self-condenses:

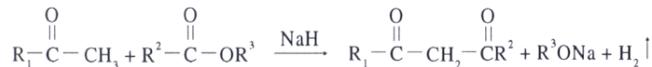


Mechanistically, the base removes a proton from the (X- position of one molecule and the resulting enolate anion then adds to the carbonyl of the second molecule. The literature includes an example (14) in which thioamide enolates are formed in high geometrical purity, resulting in diastereoselective aldol condensation:

Claisen condensation is a general term for a group of related base-catalyzed

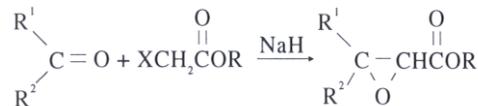


condensations of activated methylene groups with carbonyl compounds, usually referring to ester- ester or ketone-ester condensations to give 1,3-dicarbonyl compounds:

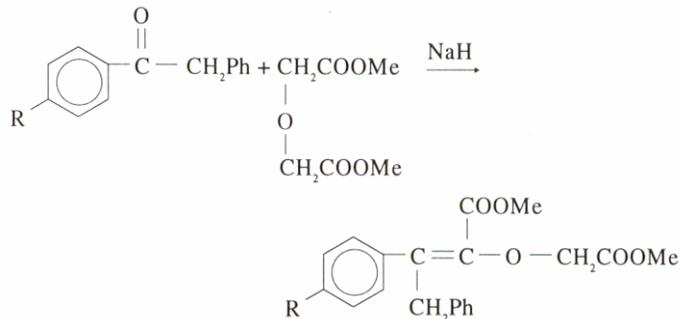


Since the reaction is reversible, formation of the desired product is favored by effective elimination of the alcohol formed as the neutralized sodium salt (R^3ONa). Sodium hydride is very efficient in this regard, as well as in minimizing side-reactions. The use of sodium hydride in Claisen condensations was pioneered by Hansley (15) and evaluated extensively in the classic article by Swamer and Hauser (16).

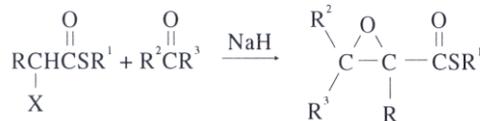
The **Darzens condensation** forms glycidic esters by reacting aldehydes or ketones with esters of α -halo-acids:



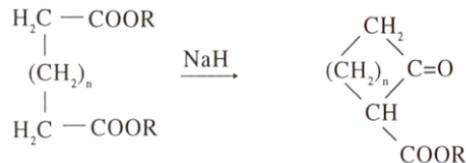
The use of sodium hydride in this reaction results in higher yields free of side reactions, relative to alternative bases. Darzens condensation has also



been applied to the preparation of glycidic thiol esters (17), where it is important to use a non-nucleophilic base:

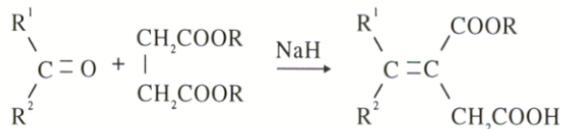


The **Dieckmann condensation** is a special case of ester condensation consisting of the intramolecular condensation of esters in polycarboxylic acids to form a cyclic β -ketoester:



The use of sodium hydride provides higher yields of three to six membered rings and also permits the formation of larger rings. Larger rings are generally unobtainable using other bases.

The **Stobbe condensation** is a special case of aldol condensation in which an aldehyde or ketone reacts with a dialkyl succinate to form a monoester of an α -alkylidene (or arylidene) succinic acid:

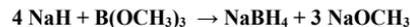


Stobbe condensation with sodium hydride has recently been applied to the condensation of aryl benzyl ketones with dimethyl diglycolate (18).

Inorganic Reactions

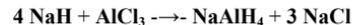
a. Hydride Preparations

Sodium hydride is one of the least expensive raw materials for the production of other hydrides. Sodium borohydride is prepared commercially by the reaction:

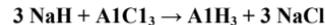


Other typical hydrides prepared from sodium hydride are:

Sodium aluminum hydride

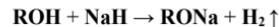


Aluminum hydride



b. Preparation of Sodium Alcoholates

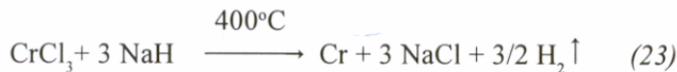
Sodium alcoholates can be prepared by the general reaction



The 60% dispersion of sodium hydride makes it possible to selectively prepare alcoholates of certain di-functional alcohols more readily than with sodium metal. When metallic sodium is used, reduction of conjugated nitrile and/or carbonyl groups such as di-functional alcohols can occur.

c. Reduction of Metal Salts

At temperatures over 300°C, sodium hydride becomes a reducing agent liberating metal or metal hydride from certain salts. For example:



At lower temperatures sodium hydride reacts more selectively than metallic sodium and has been used to remove vanadium and other impurities from titanium tetrachloride.

d. Miscellaneous

Sodium hydride dispersion is effective for removing the last traces of water, alcohol, oxygen, and some sulfur compounds from solvents and certain gases. It reacts with ammonia to form sodium amide, with carbon oxides to form products including formate and oxalate, and with sulfur dioxide to form sodium dithionite. Smalley (24) has used sodium hydride for the desulfurization of iron and steel. Its advantage over sodium metal for these reactions is that it holds its discrete particle size and reactive surface up to 400°C, while sodium melts and coalesces at 100°C unless continually redispersed.

Sodium hydride has been investigated for preventing corrosion of steel (44) and for descaling of steel and alloys (45a,45b,45c,45d). It was also found to be effective for decomposing PCB's in industrial oils (46) and in a process for conversion of bitumen to coke (47).

In recent years, Prof. Paul Caubere and others have extended the utility of sodium hydride in organic systems through work on "complex reducing agents", reducing systems composed of sodium hydride, alkoxides and metal salts (18). These reagents are active hydrogenation catalysts and also reduce aromatic halides to the hydrocarbon and ketones to alcohols, couple aromatic halides, oligomerize dienes, carbonylate halides and catalyze transesterification reactions (48a,48b,48c,48d).

4. Comparison of Bases

The advantages of NaH compared to other bases are:

- Stronger base (compared to alkoxides)
- Large excess or elevated temperatures are not needed
- Increased yields
- Forcing conditions not needed
- Side reactions eliminated
- Hydrogen evolved measures reaction extent

A comparison of bases indicates that all bases react to form a metal salt of the carbanion. Sodium hydride, lithium hydride and butyl lithium react irreversibly, forming hydrogen or butane respectively. The use of sodium metal is complicated by its tendency to produce unwanted reduced by-products. Metal alkoxides and amides react reversibly and therefore generally require excess reagent and higher temperatures. Generally, the cost of lithium bases is much higher than sodium hydride making the sodium hydride route economically attractive.

Condensation Reactions -Comparison

Claisen acylation and carbethoxylation of ketones and esters to form β -diketones and β -keto esters have generally been effected with sodium alkoxides, sodium, or sodium amide (49,50,51). Except in acylations with highly reactive esters like ethyl oxalate or ethyl formate, sodium alkoxides are not strong enough bases to produce satisfactory yields. Sodium amide is a much stronger base, but frequently attacks the carbonyl group of esters to form amides (52). The applicability of sodium in the self-condensation of esters is correspondingly limited by the tendency for bimolecular reduction with the formation of acyloins. Hansley (49,50,51) has shown that sodium hydride produces better yields than these other common reagents in certain acylations of ketones and especially self-condensation of esters. Swamer (53) has shown that sodium hydride effects the self-condensation of ethyl isovalerate which is not condensed, even with forcing

conditions, by sodium ethoxide. In contrast to sodium amide, sodium hydride does not attack the carbonyl group of esters. Self-condensations of esters are rapidly carried out with an ester-hydride ratio of one mole per mole. The general procedure of heating the ester to the temperature listed in Table 4 with the rapid addition of the sodium hydride oil dispersion gave the best results. Table 4 summarizes the comparison.

Table 4. Self-Condensation of Esters

Ester	Reagent	React. Temp., °C	React Time, Hrs	% Yield	Ref.
Ethyl Acetate	NaH Dispersion	78	1	88	
	NaOEt forced	78	8	75-76	(54)
	Na			28-38	(55,56)
Ethyl Propionate	NaNH ₂			8	(57)
	Na dispersion	100	3	100	
	NaH dispersion	95	0.75	83	
	NaOEt	95	16	46-47	(54)
	NaOEt forced	95	10	81	(58)
	NaOEt	95	16	46-47	(54)
Methyl laurate	NaOEt forced	95		81	(59)
	Na			15-32	(60)
	NaH dispersion	135	1.5	97.7	
Ethyl laurate	NaH dry, ground	125	3.9	97	(61)
	NaOEt forced	120/15mm	4	79	(49)
Methyl stearate	NaH dispersion	145	2.0	97.0	
Methyl oleate	NaH dispersion	145	2.0	98.5	
Methyl caproate	NaH dispersion	120	2.0	64.0	
Ethyl phenyl acetate	NaH dispersion	105	5.5	88.0	

With keto-ester condensations (Table 5) the procedure of first converting the ketone to be acylated to its sodio derivative and then adding the acylating ester employed previously with sodium amide (62) has generally not been satisfactory with sodium hydride, as considerable self-condensation occurs. The general method adopted for "mixed" condensations by sodium hydride consists in slowly adding the component to be acylated to a stirred suspension of sodium hydride in the acylating ester, in the presence of an inert solvent (53). The condensation thus proceeds continually as the component to be acylated is converted to its sodio derivative.

Several condensations were tested and the yields and reaction conditions found are reported in Table 5.

Table 5. Keto-Ester Condensation

Ester	Ketone	Reagent	°C	hrs)	Yield (%)
acetate	phenone	isp.	13	2	11
		round	00		39
		2	35	4	14
propionate	hexanone	isp.	13	7	10
		round	10	4	19
		2	13	2	4

In carbethoxylation of ketones, (Table 6) sodium hydride generally produces higher yields than sodium ethoxide or metallic sodium, and even somewhat better than sodium amide (65). In carbethoxylation of esters, sodium hydride yields equal those obtained with sodium ethoxide, but without the use of forcing conditions (16).

Table 6. Carbethoxylation of Cyclohexanone with Sodium Hydride and Other Common Reagents.

Condensing Agent	Reaction		% Yield	Ref.
	Time, Hours	Temp °C		
NaH	-	r.t.	37	(16)
NaH disp.	1.5	r.t.	50	
NaOCH ₃	-	-	0	(66)
NaNH ₂	2	33	18	(65)

In the Stobbe condensation side reactions encountered by the use of other reagents are considerable. For example, in the condensation of benzophenone and diethyl succinate (Table 7) with sodium ethoxide and ether, a significant amount of benzhydrol is always obtained (67). The condensation of benzophenone with diethyl succinate using sodium hydride dispersions was completed rapidly with 96% yields of 13- carbethoxy , or-biphenylvinyl acetic acid.

In the Dieckmann condensation, certain esters having an activated hydrogen on the α -carbon atom undergo intra- molecular cyclization. These reactions may be illustrated by the formation of α -carbethoxycyclopentanone from diethyladipate (Table 8). The cyclization procedure using sodium hydride dispersions is rapid and gives comparable yields to sodium metal. High temperatures and long reaction times are not needed as with other reagents and side reactions are eliminated.

Table 7. Condensation of Benzophenone and Diethyl Succinate with Base Catalysts

Reaction					
Condensing Agent	Time	Temp °C	Solvent	Yield	Ref.
NaOEt	several days not reported	room temp. 100	Et ₂ O None	60 90	(8,69) (8,69)
NaH	6 days	room temp.	EtOH	50	(8,69)
NaH disp.	8 hours	room temp.	Et ₂ O	77a	(70)
NaH disp.	1 hour	room temp.	Hexane	96	

Table 8. Comparison of Yields and Reaction Conditions in Intramolecular Cyclization of Diethyl Adipate

Reaction				
Condensing agent	Time hours	Temp °C	% Yield	Ref.
Sodium metal	7	110	74-76	(71)
Sodium amide	6	-	70-80	(72)
NaH disp.	1.5	40	65-80	

Alkylation Reactions -Comparison

The preparation of *N,N*-disubstituted amides from the *N*- substituted amide has been evaluated by Pones (73), using granular sodium hydride, with excellent results. The use of sodium hydride-oil dispersions resulted in much faster reaction at lower temperature and improved yields.

Table 9. Preparation of N-Alkyl Acetanilides with Sodium Hydride

Sensing agent	alkyl Halide	Reaction		Solvent	Yield	Ref.
		Temp °C	Time, Hours			
ground	iodide	35	10	Xylene	89	(73)
ground	bromide	35	30	Xylene	79	(73)
disp.	iodide	42	2	Toluene	100	
disp.	bromide	r.t.	4	Diglyme ^a	70	

^aDimethyl ether of diethylene glycol

The use of sodium hydride instead of metallic sodium in the preparation of the sodio derivative of acetanilide (Table 9) affords more rapid reactions and no byproducts from reaction with the halide starting materials (81,73).

Using sodium hydride dispersions with acetanilide and dibromobutane gave a better yield of *N,N'*-diacetyl-*N,N'*-biphenyl- α,ω -diaminobutane in less time. These acetylated compounds, are generally easily hydrolyzed to the amine.

In the case of secondary amines, previously used methods (69, 74, 75,55, 76, 77) frequently yield undesired heterocyclic compounds (78, 79,80).

5. Industrial Applications

Industrial applications of sodium hydride fall into categories including:

- Pharmaceuticals
- Flavors and Fragrances
- Agricultural Chemicals
- Polymerization Catalysts
- Hydride Chemicals

a. Pharmaceuticals

Polyphenyl amides, useful as anticholesteremics and anti-arteriosclerotics, were prepared from their corresponding esters in the presence of NaH (25). A base-catalyzed coupling reaction was employed to prepare aminopterin which have anti-tumor and anti-inflammatory (e.g. arthritis) activity (26). Sodium hydride was used to prepare quinoline-derived antibiotics (27). Pyridyl keto alcohol drug intermediates were produced via NaH-catalyzed aldol condensation (28). Several NaH-catalyzed asymmetric syntheses have been reported. Examples include optically active allyl alcohol intermediates (29), an intermediate used in the synthesis of duloxetine by arylation (30), azetidiones (31) and florfenicol, thiamphenicol, and chloramphenicol antibiotics (32).

b. Flavors and Fragrances

Sodium hydride was used in an alkylation reaction to prepare butyronitriles as perfume components (33) and to prepare intermediates for perfumes (34).

c. Agricultural Chemicals

Use of sodium hydride in the preparation of p-chloro-phenylcarbamic acid ester herbicides was reported (35). Uses were also described in the preparation of optically active allyl alcohol (29) and pteridine intermediates (34) for agrochemicals.

d. Polymerization Catalysts

An important commercial application for sodium hydride is as a catalyst for the preparation of polyamides by polymerization of lactams. Recent patents in this area describe finely powdered polyamides (36), lubricant-dispersed polyamides (37), carbon fiber-reinforced polyamide compositions (38a,38b), and polyamide rods having high impact strength (39). Sodium hydride catalysis has also been used for polymerization of olefins (40a,40b), vinyl chloride (41) and silanes (42a,42b) and to manufacture polyurethane binders for recording media (43).

6. Packaging

Sodium hydride is a flammable solid shipped under hazard class 4.3, "Dangerous When Wet", Packaging group I. Safety is the principal motive in Rohm and Haas Company's packaging design. Rohm and Haas' sodium hydride 60% dispersion production is automated preventing exposure to plant atmosphere during either manufacture or packaging stages. Five kilogram (5 kg) units of sodium hydride are sized, packaged and sealed under an inert nitrogen atmosphere in bags made from one of two types of plastic material. One plastic is engineered to dissolve in toluene or similar aromatic solvent, and the second to dissolve in THF or similar polar, aprotic solvent.

Two of the solvent soluble five kilogram units are placed in an intermediate thermally sealed PE package. Multiples of these 2 x 5 kg units are contained in steel drums suitable for overland and ocean shipping. In the case of toluene soluble packaging, nine of the 2 x 5 kg intermediate packages are contained in each drum and for THF soluble packaging, eight of the 2 x 5 kg units are in each drum. Each drum is further provided with a tertiary PE lining sealed with a plastic locking tie. Packages designed for air freight contain three 5 kg units in secondary, thermally sealed PE packaging and a tertiary pail liner.

Rohm and Haas recommends that sodium hydride be consumed in multiples of discrete packaging units. Most preferable is to use an entire drum or pail quantity. If that is impractical, use quantities should coincide with the intermediate packaging of 2 x 5 or 3 x 5 kg quantities and if that is not possible, then multiples of the five kilogram unit should be used to establish batch size.

The partial use of a 5 kg solvent soluble package is not recommended. However, if there is no way to avoid this, containers should be quickly returned to controlled storage conditions after observing the following procedure.

Immediately flush the partially filled solvent soluble bag and/ or intermediate PE packaging unit. Tightly re-seal each plastic packaging unit (including the tertiary PE liner) with a suitable rope, wire, or locking plastic sealing device. Flush the partially filled drum or pail with dry nitrogen, replace the cover, and secure with the lid retaining ring.

7. Safety and Handling

Rohm and Haas Company is committed to facilitating the safe use and handling of sodium hydride. This brochure is provided for the purpose of supporting applications development and is not intended to serve as a safety resource. Please refer to the following safety resources when there is a question regarding safety:

Sodium Hydride Material Safety Data Sheet

Sodium Hydride Safety Brochure

Sodium Hydride Safety Video

Sodium Hydride On-site Safety Seminars and Safety Audits

Sodium Hydride Assay Method

Should any questions regarding safe handling issues remain after review of these resources, consult one of Rohm and Haas Company's technical support specialists via the contact information at the end of this brochure.

References

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