

How to Determine the Dangerous Properties of Substances

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ABSTRACT

Fire and explosions may develop into catastrophes when dangerous substances are transported. A sound knowledge of the dangerous properties of the substances to be transported is therefore of major importance. This knowledge should be the basis for the classification of dangerous goods and for other international regulations that concern the transport of these substances. This paper contains a rough survey of the principles involved in the classification of dangerous goods as well as discussions on fire and explosion hazards of dangerous goods, and the phenomena (mechanisms, physical effects, sensitivity, etc.) that play an important role in unwanted explosions. The state of the art will also be reviewed concerning the classification of dangerous goods. This review will center around the United Nations recommendations on which a growing number of national and international regulations are based in countries all over the world. Attention will also be paid to laboratory scale investigations of the hazardous properties of substances and to the first results of a comparison of the different test methods proposed for classification of organic peroxides. Also, some tests will be reviewed on intermediate and full scale bases. The last section of this paper will be dedicated to some recent investigations on the self-heating of bulk materials.

Incidents may develop into catastrophes when dangerous goods are being transported. The circumstances under which this can happen depend strongly on the properties of the substance, the packagings used, and the environment around these packagings at the moment of the incident. The formation of combustible gases in a mass of coal can, for instance, give rise to an explosive gas-air mixture in a bulk carrier, but this cannot happen in a railway wagon because of the greater ventilation. The increase in strength of packagings will decrease the chance and the size of dangerous leaks for toxic materials but can turn a mild thermal explosion of an organic peroxide into a serious one. A sound knowledge of the dangerous properties of substances to be transported is therefore of major importance for the safe transport of substances.

DIFFERENCES BETWEEN DANGEROUS PROPERTIES

Considering the titles of the different classes (radioactive materials are not taken into consideration) used for the classification of dangerous substances, it would be thought that the differences between these substances are only based on the physicochemical effect that can be produced (1). There is, however, a second way of differentiating between these substances based on the interaction between them, the casing of the substance, and the environment surrounding this containment.

If the casing in which the substance is trans-

ported is considered (e.g., a tank container or a packaging), it can be stated that this casing has a dual function: it serves as a barrier against the release of the substance and as a protection against influences from the outside. For most of the dangerous substances, a disruption of this barrier is necessary for the substance to become a hazard to the surroundings (Category 2 substances). For some other dangerous substances, even the disruption of this barrier is not enough for the substance to become a hazard because it needs additional contact with other substances (Category 3 substances). These substances are, finally, substances that harbor an intrinsic hazard--they can disrupt their casing by the physicochemical effect (Category 1 substances).

Examples of the different categories are:

1. Explosives and substances with explosive properties such as organic peroxides and other self-reactive substances;
2. Toxic and infectious substances, flammable gases, and vapors;
3. Oxidizers and substances that, when they come into contact with water, emit flammable gases.

Measures to prevent accidents or minimize their effects are different for the three categories. For substances that can detonate (part of Category 1 substances) dilution could exclude this effect. In the case of chemicals, this may be possible, but not for explosives because these substances will no longer function. Segregation regulations prevent

oxidizers (Category 3) from coming into contact with combustibles.

It can be generally said that for the prevention of accidents of Category 1 substances, one has to consider the substance properties in the casing in combination with the environment that is to be expected. Tests on a laboratory scale, which will sometimes include packaged materials, are therefore indispensable. A change of casing may give rise to a change in the behavior of the substance. For Category 2 substances, the behavior of the filled casing in its environment has to be examined. A change of casing will not change the behavior of the substance (only the amount in case of a spill). For Category 3 substances, the same holds as for Category 2 substances with the provision that a leak will not invariably lead to the occurrence of a physico-chemical effect because additional substances are necessary for this. Moreover, additional rules for segregation may more adequately prevent accidents with this type of substance.

TYPES OF EXPLOSION

A distinction is usually made between physical and chemical explosions. An example of a physical explosion is the bursting of a steam boiler. A chemical explosion occurs as a result of a chemical reaction in a substance through which energy (heat) is set free and hot, normally gaseous reaction products are formed. Fire phenomena need not necessarily occur, but the reaction products are usually flammable. An investigation into the possibility of a chemical explosion of a substance will have to be aimed in particular at the chemical properties of this substance, specifically at whether the substance can undergo a conversion during which energy is set free. Whether a chemical explosion has a destructive effect is dependent on the reaction rate and on the amount of gas formed during this reaction. Further, the situation in which the substance is kept is of paramount importance. Examples of chemical explosions follow.

Thermal

Self-heating (exothermal decomposition) occurs when a substance is stored or processed at a high enough temperature that the chemical reaction of the substance under these conditions causes a heat generation that exceeds the heat losses. The risk of self-heating will increase with increasing quantities. If self-heating of the substance occurs locally (e.g., in a solid), this may ignite a fire or explosive burning. Homogeneous self-heating (e.g., in a liquid) may give rise to a thermal explosion, in which case all parts of the substance will react simultaneously and at approximately the same rate. The effect of the thermal explosion is strongly dependent on the nature of the situation and of the substance involved.

The main properties of a thermal explosion are (a) no defined reaction zone will exist but self-heating and self-accelerating decomposition throughout the substance will occur; and (b) an induction period (i.e., time to explosion) that is dependent on kinetics and heat losses must be present.

Explosive Burning (Deflagration)

When a substance comes to a reaction as a result of local heating and this reaction is maintained by the formation of a reaction zone that travels through

the substance without the addition of oxygen from the air, it is known as explosive burning or deflagration of the substance. The reaction zone travels through the substance by means of heat transfer. The rate at which this takes place is referred to as the linear rate of burning. The linear burning rate increases with increasing pressure. Deflagration can therefore result in a violent explosion particularly in confined situations. Deflagration, which sometimes looks like an ordinary fire, cannot be extinguished by excluding air, but can be extinguished by effective cooling of the reaction zone, for instance with water.

Special attention is required in the case of deflagration of gas- and dust-air mixtures, referred to as gas and dust explosions. In these cases a mixture of flammable gas, vapor, or dust with air is being dealt with, for which there are lower and upper explosion limits. Below the lower explosion limit, there is a shortage of flammable material, and above the upper explosion limit, the inhibiting effect of the excess fuel prevents flame propagation. The explosive region lies between these explosion limits. The minimum energy that is required to ignite an explosive gas-, vapor-, or dust-air mixture is called the minimum ignition energy.

Therefore, the main properties of explosive burning (deflagration) are (a) a propagating reaction zone will exist with linear rates of burning between 10^{-5} and 100 m/sec (depending on pressure and temperature); (b) energy will be transferred ahead of the reaction zone by conduction, convection, or radiation; (c) most deflagrating substances are readily ignitable; and (d) the effect of deflagration is dependent on confinement.

Detonation

If a substance is locally brought to reaction by a shock and this reaction is maintained by the formation of a reaction zone that travels through the substance at supersonic speed, the substance is said to be detonated. The reaction zone travels by means of a shock wave through the substance. A distinction should be made, however, between the possibility of detonation and the sensitivity to detonation. A detonation always has a strong destructive effect. In the case of explosives, use is made of this effect. A shock wave is created in the surrounding air that is heard as a bang. Sometimes a deflagration can result from a detonation, as well as in the cases of gas and dust explosions.

The main properties of detonations are (a) a propagating reaction zone will exist with detonation velocities from 1000 to 9000 m/sec; (b) energy will be transferred by shock compression of from 25 to 400 kbar; (c) most detonating substances have low initiation sensitivity; and (d) the effect of detonation will be destructive and in most cases independent of confinement.

STATE OF THE ART IN CLASSIFICATION

The rules for classification of explosives and substances that can possess explosive properties are progressing. The UN already accepted a flow chart (1) for explosive (class 1) some years ago and recently completed the test descriptions and criteria that are to be used for the classification of explosives. For sea and air transport, the International Maritime Organization (IMO) and International Civil Aviation Organization (ICAO) will probably accept the UN test methods and criteria. The European regulations for rail (RID), road (ADR), and inland water-

way transport (ADNR) which, at the moment, are based on quite different classification procedures, will move toward the UN system. A new draft of class 1 of RID-ADR, based on the UN scheme, is already under discussion. A change toward the UN system has also been observed recently in Europe for regulations on storage of explosives. However, the European Economic Community (EEC) decided 2 years ago to use the RID-ADR system for their directive on hazardous chemicals.

For substances of classes other than class 1, which may have explosive properties, class 5.2 (organic peroxides) plays the leading role in the UN system. The developments in class 5.2 are used for substances of other classes. The UN Committee of Experts recently accepted a flow chart for the organic peroxides. The next step will be the acceptance of test methods and criteria. This must not take too much time because in Europe a new draft of class 5.2 regulations of RID-ADR based on the UN class 5.2 is already available and the discussions on this draft have already started. It is hoped that the UN classification system can stay ahead so as to arrive at one system for all modes of transport, followed by other national and international regulations. If all classification systems were based on one system, an improvement in international cooperation and an elimination of trade barriers would be achieved.

For the acceptance of test methods it will be necessary to exchange information between different laboratories. A first step was made by organizing a seminar on test methods for organic peroxides at the Dutch Institute for Applied Scientific Research (TNO) in October 1984, which was followed by a second seminar in Washington, D.C., in May 1985. During the first seminar, the idea arose to start a data base for all useful test results of the organic peroxides listed in the UN recommendations (1). Such a data base will be a useful tool for the comparison of the test methods and the allocation of criteria to the tests. The sequence of results will show whether by using different test methods the same property of the substances can be determined. Further, it can be used for setting the criteria for subdivisions at the same level.

The data base is currently in operation and about 5,000 test results of the approximately 130 entries for organic peroxides in the UN recommendations have been introduced from about 20 laboratories in Europe, the United States, and Japan. The next step will be to compare the results and to look into possible causes of differences. It is plausible for instance, that an organic peroxide diluted with volatiles will behave differently in closed and open vessels because of evaporation. The properties introduced in the data base are:

- Detonation
- Deflagration
- Mechanical sensitivity
- Heating under defined confinement
- Explosive power

Results have been collected for about 35 test methods (2). A number of these tests are also used for testing explosives. Also, some tests for the determination of properties of packaged organic peroxides are part of the data base.

LABORATORY SCALE TESTS

The determination of the properties of explosive substances with the aid of laboratory scale tests is predominantly work for specialists in specialized

laboratories. Some tests contain so much material to be tested that the effect equals trinitrotoluene explosions of several kilograms. By contrast some tests are performed on a milligram scale. A few examples of tests may serve to give an idea of the type of tests that are to be performed.

The first type of test is the tube test shown in Figure 1. Several tube tests are in use in different parts of the world and the one shown is the TNO 50/70 tube test. The test is performed in a very strong steel tube in which the substance is put in contact with a high explosive charge. This charge is detonated and with the help of a measuring wire in the axis of the tube, the velocity of the front is measured. If the tube is fragmented or empty after the test and the measured reaction velocity exceeds the sound velocity, the substance can detonate. An example of fragments of a tube after the test is completed is shown in Figure 2, which also shows the results of a detonation of a specific sample of ammonium nitrate prills.

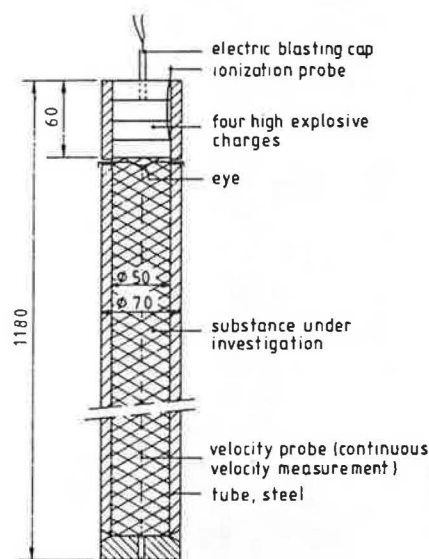


FIGURE 1 TNO 50/70 tube test.

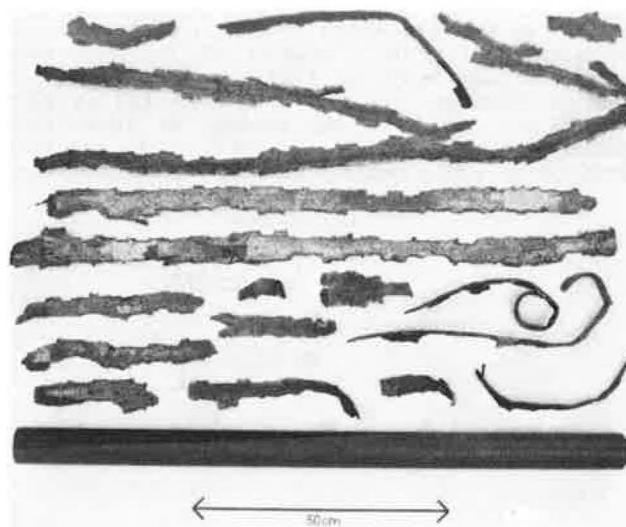


FIGURE 2 Results of a detonation in a tube test.

With the Dutch pressure vessel tests (see Figure 3) the effect of external heating on a substance is determined. The vessel has a capacity of 0.2 L and is closed at the top with a standardized membrane. Further, the vessel is provided at the side with a venting device. Ten grams of a substance are heated in a programmed way in the vessel and the effect is observed. In case the membrane remains intact, a second test is performed with the next smaller vent hole and vice versa.



FIGURE 3 Dutch pressure vessel test.

By using this procedure, the limiting diameter is determined, which is a measure of the substance behavior during external heating. The larger the limiting diameter, the more dangerous is the substance. There are, at the moment, at least four different versions, all developed from the original Dutch version. This calls for standardization. Figure

4 shows the BAM friction machine in which the sensitivity to friction of a small portion of a substance is tested between a porcelain plate and a porcelain peg. The load on the peg can be varied and the limit determined at which point a positive report can barely be perceived.

TESTS IN PACKAGINGS

As mentioned before, in some cases the behavior of a substance in a package also has to be determined. Various tests are being developed for this purpose. The next test to be discussed is used for substances that have a high value in tests that involve the effect of external heating, such as the pressure vessel test. Depending on the type of packaging, it may be possible to suppress the explosive properties of the substance to a level at which it no longer explodes in practice. Because the packaging plays a decisive role in this context, the test should be performed in the actual packagings. Figure 5 shows the test set-up with a composite packaging filled with an organic peroxide. The peroxide is heated with an electric coil inside the liquid until the thermal explosion follows. During this explosion, a cloud is formed that, in the case of some peroxides, ignites spontaneously. Figure 6 shows the result of this test with a mild exploding peroxide (upper) and the result of a very fast exploding organic peroxide (lower). The latter explosion is so violent that it fragments the weak packaging. If an aluminum can is used instead of the composite packaging, which means much more confinement for the explosion, dangerous fragmentation will be observed (see Figure 7). At the moment, the UN recommendations indicate that organic peroxide-packaging combinations may only be shipped without an explosives subsidiary risk label if tests have shown that the peroxide cannot explode in the specific packaging.

INTERMEDIATE SCALE INVESTIGATIONS

One of the main design criteria for tanks and tank containers for the transport of organic peroxides is that the tank must not explode in the case of complete fire engulfment over a period of 1 hr. Because this criterion is not easy to meet with reactive liquids such as organic peroxides, investigations have been performed at the TNO to derive scaling laws.

Different organic peroxide formulations have been tested in tanks of 8, 33, and 234 L. During these tests, the vent areas have been varied and the internal pressure in the tank has been measured while the tank was heated by a representative fire on the outside. Figure 8 shows a view during a test with the 234-L tank, and Figure 9 shows the results

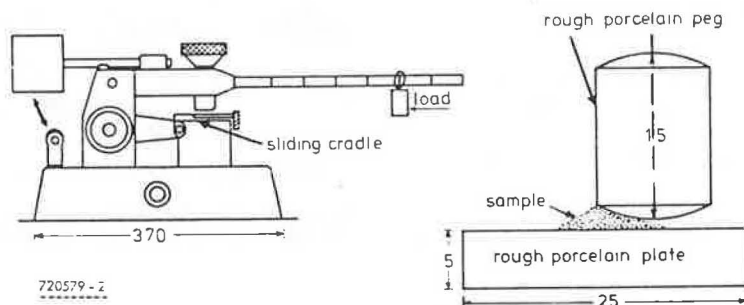


FIGURE 4 BAM friction apparatus.

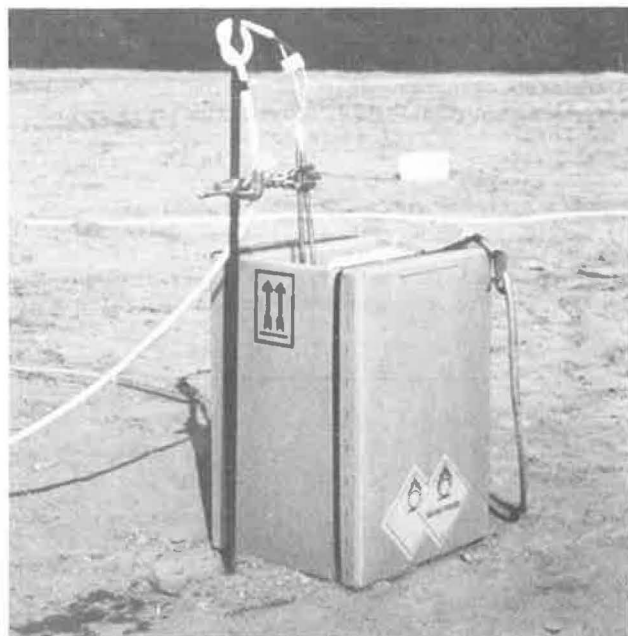


FIGURE 5 Test set-up.



FIGURE 6 Effect of a mild (*top*) and fast (*bottom*) exploding organic peroxide.

of a test series for an organic peroxide in the 33- and 234-L tanks (3).

BULK TRANSPORT OF DANGEROUS SUBSTANCES

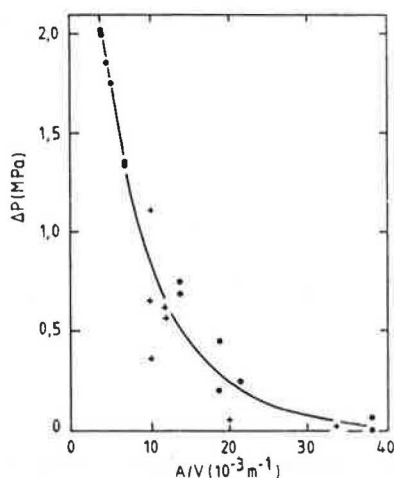
For some substances transported in bulk, self-heating may cause dangerous situations. Investigations as early as 1965 at TNO showed that an improperly produced (overly acid) fertilizer can cause such temperature rises as a result of self-heating and self-ignition followed by a deflagration of the fertilizer. The foundering of the merchant vessel *Sophocles* could be attributed to this effect. In ammonium nitrate fertilizers, an ample amount of



FIGURE 7 Fragments of an aluminum can after a thermal explosion.



FIGURE 8 Test with an organic peroxide in a 234-L model tank; the bursting disc has functioned and decomposition gases are being vented.



Note: A = vent area, V = volume; · = result of a 33-1 tank; and + = result of a 234-1 tank.

FIGURE 9 Maximum overpressure inside the tank as a function of the relief capacity A/V.

oxygen for the combustion reaction is present in the ammonium nitrate molecule. This is not the case in substances like coal, direct reduced iron (DRI), and tapioca. However, this does not imply that self-heating in these substances is not possible. In these events, oxygen from the air is used for the exothermal reaction.

The self-heating process in such bulk cargoes is very complex, however. The effects of particle size, chemical composition, degree of degradation, adsorbed oxygen, changing oxygen content in the surrounding air, suppletion of oxygen, ventilation, evaporation of moisture, and subsequent condensation at another place will all play a part. In the Netherlands, the self-heating process of coal has been studied for years and this study is continuing. The program consists of three parts: (a) laboratory scale investigations (TNO), (b) development of a mathematical model (TNO), and (c) measurements in coal piles (Inspection Service for Electrical Equipment in the Netherlands).

Figures 10 and 11 show some typical results of

the laboratory measurements (4-6). The study centers on the self-heating process of subbituminous coal types because these are most frequently used in coal-fired furnaces. Heat generation of the various coal types investigated showed that variations of more than a factor of 5 are not uncommon. The results of the laboratory tests are used in the mathematical model. The calculated values compare very well with temperature measurements in actual coal piles (7).

Figure 12 shows the results of calculations of the maximum temperatures in two piles of the same size that contain coal with different moisture contents. It may be concluded from the calculations

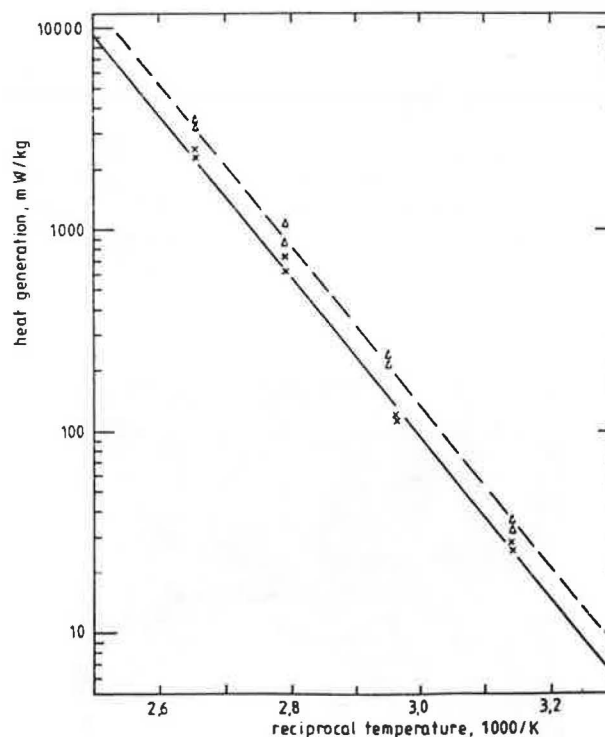


FIGURE 10 Heat generation at different (reciprocal) temperatures in an Australian (X) and an American (Δ) subbituminous coal.

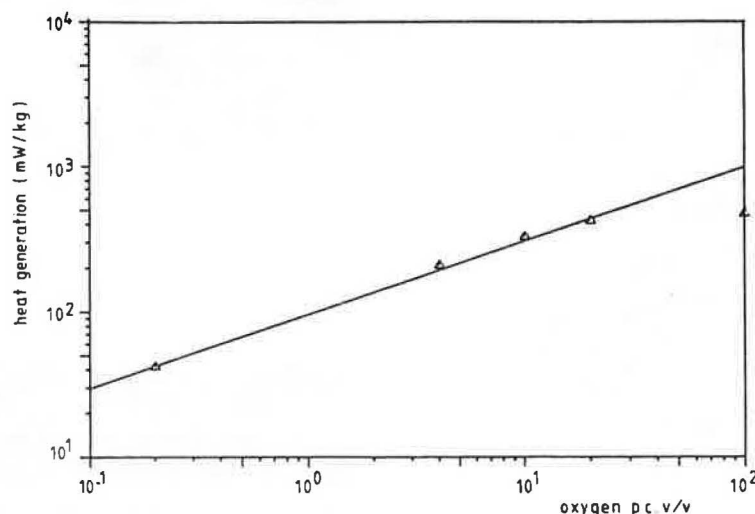


FIGURE 11 Heat generation at different oxygen concentrations in an Australian subbituminous coal at 338° K.

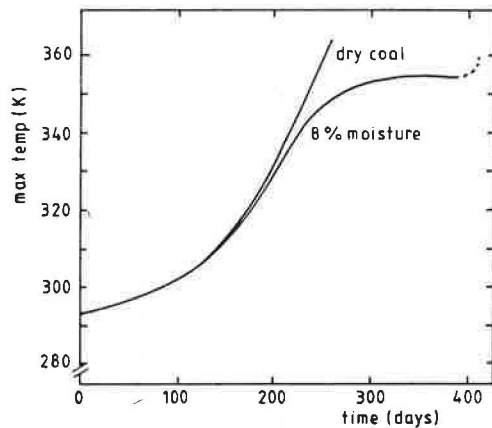


FIGURE 12 Maximum temperature in a pile of coal for different moisture contents.

that the porosity of the pile is a very important variable that affects the thermal behavior of the pile as well as the airflow through it. An obviously high degree of compaction will prevent self-heating as well as other methods of limiting the air flow.

Investigations of tapioca and DRI are still in the exploratory stage. Isothermal and adiabatic storage tests with tapioca show again the major role of moisture on the self-heating process. Because the heat production of tapioca with 14 percent water (equilibrium moisture content at about 20°C) is much higher than that of dry tapioca, it may be concluded that water also plays a direct role in the oxidation process. At elevated temperatures, the moisture content of the tapioca will decrease by evaporation. This evaporation consumes heat, which then decreases the rate of temperature rise. As soon as the temperature exceeds about 90°C, the self-heating process

will quickly accelerate to the point of local self-ignition.

Preliminary investigations into the self-heating process of DRI revealed that the combination of moisture, oxygen, and surface area is mainly responsible for the course of the oxidation process. Water (either liquid or vapor) is largely involved in the chemical reactions. Depending on the amount of water that is present, the heat generation may readily increase by a factor of more than 20. Continued investigations and efforts are necessary to obtain more information on the effect of preventive measures.

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