Letter

Relationship between accidents involving spontaneous ignition of nitric acid esters and weather conditions

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Abstract

The weather conditions at the times of accidents involving the spontaneous ignition of nitric acid esters and products based on them were analyzed. When the daily maximum temperature and average relative humidity in the 30 days preceding the accident were examined, it was found that 25 accidents out of the 34 accidents analyzed occurred when the daily maximum temperature was approximately 30°C for more than ten consecutive days or when the daily maximum temperature increased over 5–10 days to reach a value of 30°C on the day of the accident. However, the hourly changes in temperature and relative humidity in the 24 hours preceding the accidents indicated that accidents did not always occur when the temperature or relative humidity reached their maximum of the day. From the data on the daily absolute humidity changes for the 30 days preceding the accident, it was found that 27 of the 34 accidents analyzed occurred when the absolute humidity had been constant at 20 $g{\cdot}m^{-3}$ or approached this value at the instant of the accident. In addition, in 12 of the 16 accidents analyzed, in the 24 hours preceding the accidents, the absolute humidity either increased to or had been constant at approximately 20 $g{\cdot}m^{-3}$ before the accident.

Keywords : nitrocellulose, celluloid, spontaneous ignition, self-ignition, degradation

1. Introduction

Nitric acid esters such as nitrocellulose (NC) are widely used as raw materials for the manufacture of celluloid products, films, lacquers, propellants, and explosives. However, they have the capacity for spontaneous ignition, which causes many accidents. In terms of the mechanism, it is known that the cleavage of the $O\text{-}NO_2$ bond by heat and hydrolysis leads to the degradation or spontaneous ignition of nitric acid esters[1].Hence, it is thought that the weather conditions (temperature and humidity) may contribute to the occurrence of spontaneous ignition accidents.

The relationship between weather conditions and spontaneous ignition accidents involving nitric acid esters has been investigated in previous studies. For instance, for such accidents that occurred during the period 1945–1965, Nonomura[2] investigated the ambient temperature and relative humidity on the days of the accidents. The author found that the accidents occurred when the daily maximum temperature and average relative humidity were greater than 30°C and 60%, respectively. In addition, Kitagawa[3] examined in detail the temperature and relative humidity changes in the 30 days preceding the serious accident that occurred in Japan on July 14, 1964. The author found that the day of the accident was hotter than the previous 30 days. However, since this study investigated only one accident, the relationship between the temperature and humidity changes and such accidents could not be clearly understood.

Kitagawa's study motivated us to study the

Table 1 Summary of accidents considered in the present study involving the spontaneous ignition of nitric acid esters and products based on nitric acid esters.

No.	Date and Time	Location	Involved substance and its amount	Ref.
1	Aug. 20, 1927.	Tokyo	Celluloid	4)
2	Aug. 22, 1932. Around 22 : 00	Okayama	NC	3)
3	Aug. 22, 1937. Around 18 : 10	Tokyo	NC used for painting	3)
4	May9,1939.	Tokyo	Celluloid scrap	4), 5)
5	Jul.2,1940. Around4 : 30	Tokyo	Paper−like NC (200 kg) packed in shoe bags	3)
6	Aug. 19, 1940. Around 17 : 30	Osaka	Celluloid or its feedstock	3)
7	Sep.6,1944. Around 15 : 26	Osaka	NC	3)
8	Aug. 30, 1947. Around 17 : 40	Osaka	NC (300 kg) and celluloid scrap (1t)	3)
9	Sep.7,1949.	Tokyo	NC stored in the magazine	4)
10	Aug. 11, 1950. Around 23 : 00	Tokyo	NC used for painting	3)
11	Sep. 19, 1962. Around 22 : 24	Tokyo	NC wetted by 25% of alcohol (12 kg)	3)
12	Sep. 14, 1963. Around 12 : 48	Tokyo	NC stored in a lacquer−producing plant	3)
13	Jun.4,1964. Around 18 : 58	Tokyo	NC used for painting	3), 6)
14	Jul. 14, 1964. Around 21 : 56	Tokyo	NC (195t)	3)
15	Aug.6,1964. Around 17 : 03	Tokyo	NC in a store building in an electric company	3)
16	Jul. 30, 1965. Around 18 : 45	Tokyo	Manicure	3)
17	Sep. 12, 1966.	Kanagawa	Celluloid	6)
18	Sep. 25, 1966. Around4 : 06	Tokyo	NC stored in a plant that produced water−based paint	3)
19	Aug. 15, 1967.	Kanagawa	Celluloid	6)
20	May2,1969.	Tokyo	NC	6)
21	Jul. 19, 1970.	Kanagawa	X−ray film	6)
22	Jul. 31, 1971.	Tokyo	Celluloid	6)
23	Jul. 16, 1975.	Kanagawa	NC	6)
24	Jul. 18, 1975.	Kanagawa	NC	6)
25	Aug. 19, 1975.	Tokyo	Celluloid debris used as an artificial limb socket	6)
26	Aug.1,1979.	Tokyo	Celluloid	6)
27	Jul.6,1984.	Tokyo	Celluloid	5)
28	Jul. 17, 1984.	Tokyo	Celluloid	5)
29	Aug.1,1984.	Tokyo	Celluloid	5)
30	Aug.4,1984.	Tokyo	Celluloid	5)
31	Sep.3,1984. Around 15 : 00	Tokyo	Approx. 3000 movie films stored in an art museum	5), 6)
32	Jul. 16, 1996.	Ibaraki	Celluloid chips used for toy fireworks	6)
33	Aug.1,2000. Around 22 : 09	Aichi	Smokeless powder (7.7 t)	6)
34	Aug. 13, 2005. Around 10 : 09	Aichi	Wet NC used as smokeless powder (28 t)	6)

temperature and humidity changes for other accidents involving the spontaneous ignition of nitric acid esters. In the present study, we investigated the temperature and humidity changes for accidents that occurred in Japan from 1927 to 2005.

2. Research procedure

From the literature[3)−6)], 34 accidents thought to have involved the spontaneous ignition of nitric acid esters or products based on them were chosen. These accidents are summarized in Table 1.

The daily maximum temperature and average relative humidity in the 30 days preceding each accident and the hourly temperature and relative humidity in the 24 hours preceding each accident were obtained from the Japan Meteorological Agency[7), 8)]. Since weather data for the exact locations of the accidents could not be obtained, the weather data recorded at meteorological observatories close to the locations were used for this investigation. Therefore, this study is based on the hypothesis that the weather conditions at the nearby meteorological observatories were identical to those at the actual locations concerned.

3. Results and discussion

3.1 Temperature changes before the accidents

The daily maximum temperature data for the 30 days preceding the accident were examined and divided into four major patterns. The patterns are shown in Figures 1 a−1d. In these figures, the horizontal axes indicate the number of days preceding the accidents (e.g., "0" is the day of the accident and "−1" is the day preceding that of the accident).

Figure 1a corresponds to a pattern where the daily maximum temperature is approximately 30°C for more than ten days prior to the accident, and Figure. 1b shows a pattern where the daily maximum temperature gradually increases for 5−10 days before the day of the accident, reaching approximately 30°C on the day of the accident. Twenty-five of the 34 accidents analyzed conform to one of these two patterns. Figure 1c displays a pattern where the air temperature varies enormously throughout the 30

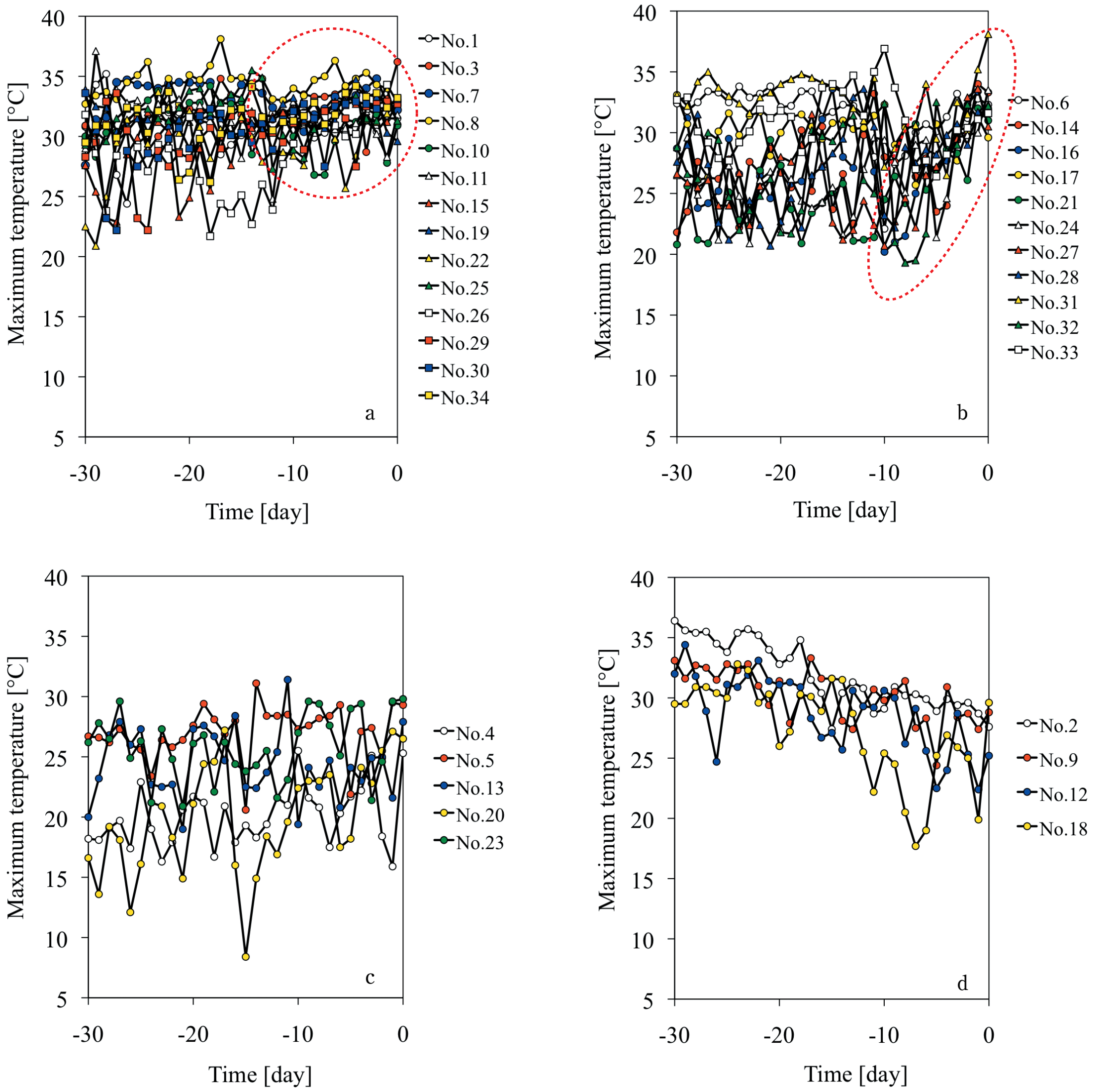

Figure 1 Changes in the daily maximum temperature for the 30 days preceding the accidents.
Pattern a : The daily maximum temperature is approx. 30°C for more than 10 days before the accident.
Pattern b : The daily maximum temperature gradually increases for 5–10 days before the accident.
Pattern c : The daily maximum temperature varies enormously during the 30 days before the accident.
Pattern d : The daily maximum temperature gradually decreases before the accident.

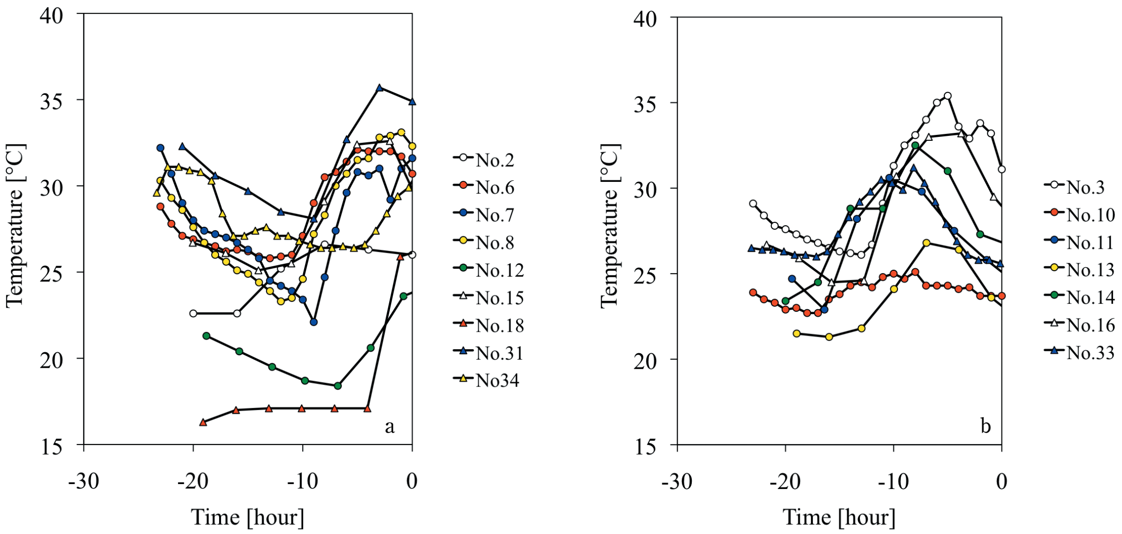

Figure 2 Changes in the hourly temperature on the days of the accidents.
Pattern a : The temperature is increasing or is the maximum temperature of the day when the accident occurs.
Pattern b : The temperature is decreasing when the accident occurs.

days. While the accidents following this pattern do not appear to be related to temperature changes, it is seen that the temperature on the day of the accident is higher than on the preceding days (1−3 days). Figure 1d shows a pattern where the daily maximum temperature gradually decreases before the accident. Only four of the 34 accidents show this pattern. From these results, it is concluded that the temperature is probably related to the likelihood of accidents occurring.

Next, we examined the temperature changes in the 24 hours preceding the 16 accidents for which the exact time of occurrence was known. The results are shown in Figures 2a and 2b; the horizontal axes indicate the number of hours before the accidents (e.g., "0" indicates the accident time and "−1" indicates the hour preceding the instant of the accident).

Figure 2a shows the temperature changes for accidents that occurred when the temperature on the day of the accident was at its maximum. On the other hand, Figure 2b shows the temperature changes for accidents that occurred after the maximum temperature had been reached. From these results, it is apparent that the accidents did not always occur when the temperature was at its maximum for the day. In particular, the majority of the accidents analyzed occurred at night. Therefore, it can be said that no definite relationship was observed between the accidents and the hourly temperature changes during the 24 hours preceding the accidents, whereas the data on the daily temperature changes for the 30 days preceding the accidents suggest that the temperature does contribute to the occurrence of accidents, as mentioned above.

3.2 Relative humidity changes before the accidents

The changes in the daily average relative humidity for the 30 days preceding the accidents were investigated. In a similar way to the temperature study, we attempted to divide the relative humidity changes into four patterns. However, in 18 of the 34 accidents analyzed, the relative humidity varied enormously during the 30 preceding days or gradually decreased before the accidents. While the data for some accidents suggested an effect of humidity changes (such as Figures 1a or 1b), these were not in the majority.

When the hourly relative humidity was examined, it was found that nearly half of the analyzed accidents did not occur when the relative humidity was at its maximum on the day of the accident. This result is similar to that found for the temperature data. From these results, no clear relationship was observed between the occurrence of accidents and the relative humidity changes.

3.3 Absolute humidity changes before the accidents

The relative humidity is the ratio of the amount of water vapor in the air to the amount of saturated vapor; this means that the relative humidity is not related to the concentration of water vapor in the air. Thus, we considered that if water vapor contributed to the reaction responsible for the spontaneous ignition accidents, then the water vapor concentration, i.e., the absolute humidity, should be correlated with the occurrence of accidents. On the basis of this assumption, the relationship between the absolute humidity calculated by Tetens' formula[9] and the occurrence of accidents was investigated.

The absolute humidity changes for the 30 days preceding the accidents were divided into four patterns, as shown in Figures 3a−3d, similarly to the temperature data. Twenty-seven of the 34 accidents analyzed belonged to two patterns: one in which a high absolute humidity was maintained for more than ten days before the accident, and the other in which the absolute humidity increased for 5−10 days before the accident (Figures 3a and 3b, respectively). In the case of some accidents, the absolute humidity varied enormously during the preceding 30 days (Figure 3c); however, these accidents were characterized by the absolute humidity on the day of the accident being higher than that over the previous 1−3 days. Only two accidents could not be classified as one of these patterns (Figure 3d). These results show that the nitric acid esters had been exposed to high concentrations of water vapor for a finite period before most of the accidents analyzed.

The absolute humidity in the 24 hours preceding the accidents was investigated for the 16 accidents for which the exact time of occurrence was known. It was observed that the absolute humidity increased or remained constant at approximately $20\,g{\cdot}m^{-3}$ for 12 of the 16 accidents, as shown in Figures 4a and 4b. As described above, when the temperature and relative humidity changes in the 24 hours preceding the accident were investigated, it was found that not all the accidents corresponded to the maximum temperature or maximum relative humidity on the day. On the other hand, in the case of absolute humidity, most of the accidents were found to have occurred when the absolute humidity had been constant at approximately $20\,g{\cdot}m^{-3}$ or increased to approximately $20\,g{\cdot}m^{-3}$ during the 24 hours preceding the accident. These results indicate that water vapor strongly influences the degradation or spontaneous ignition of nitric acid esters.

4. Conclusion

(1) An examination of the daily maximum temperature for the 30 days preceding accidents involving nitric acid esters showed that in 25 of the 34 accidents analyzed, the daily maximum temperature was either approximately 30°C for more than ten days before the accidents, or gradually increased to reach approximately 30°C before the accidents. On the other hand, analysis of the temperature changes in the 24 hours preceding the accidents indicated that not all the accidents occurred at the maximum temperature on the day of the accident.

(2) The daily average relative humidity varied enormously during the 30 days preceding the accidents; this variation was much greater than that found in the temperature data, and no specific tendency was observed. When the relative humidity changes in the 24 hours preceding the accidents were examined, it was seen that

393

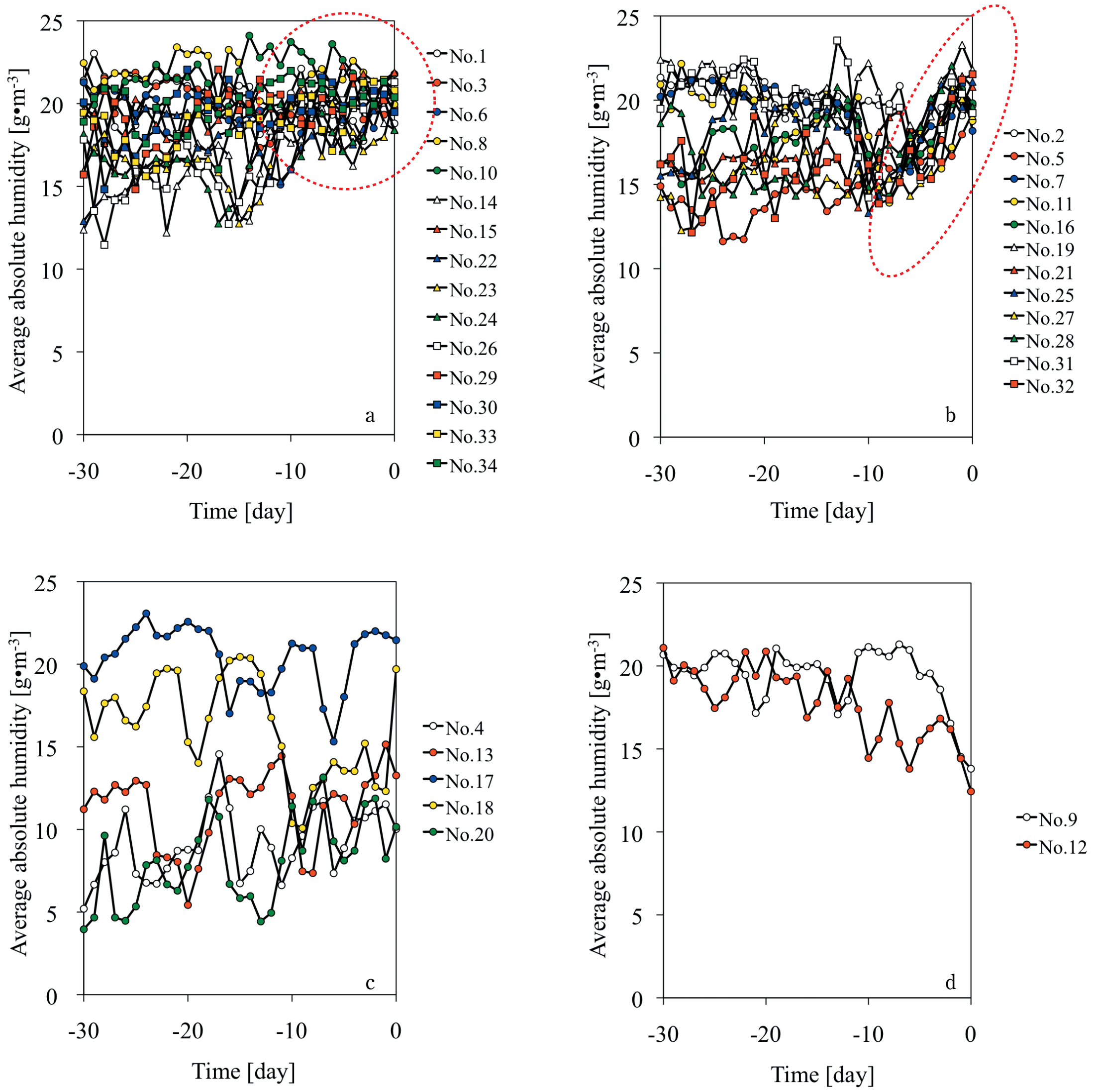

Figure 3 Changes in the daily absolute humidity for the 30 days preceding the accidents.
Pattern a : The daily absolute humidity is approx. 20 g·m^{-3} for more than 10 days before the accident.
Pattern b : The daily absolute humidity gradually increases for 5–10 days before the accident.
Pattern c : The daily absolute humidity varies enormously during the 30 days before the accident.
Pattern d : The daily absolute humidity gradually decreases before the accident.

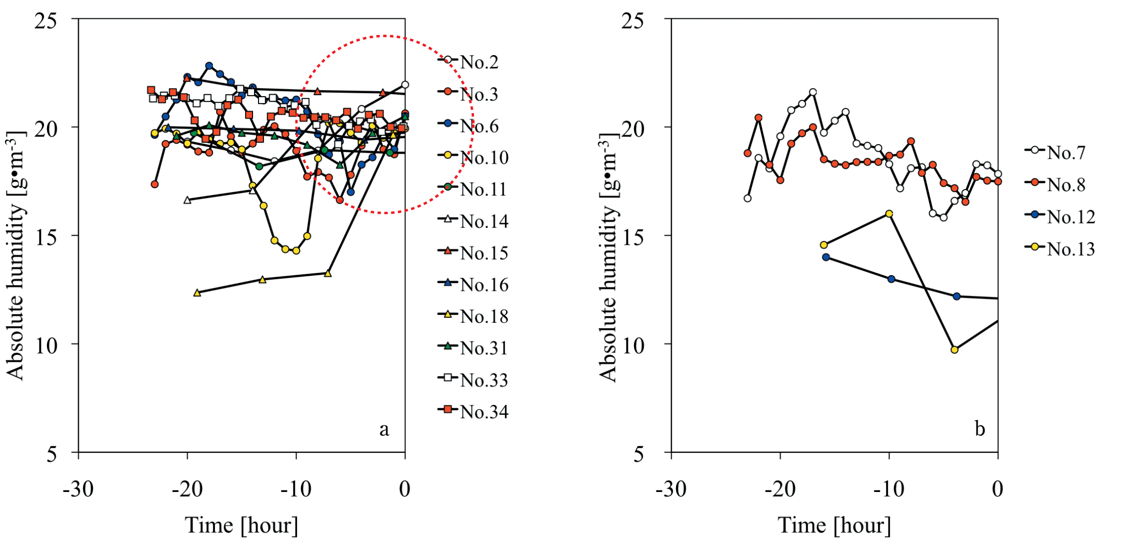

Figure 4 Changes in the hourly absolute humidity on the days of the accidents.
Pattern a : The absolute humidity is increasing or is the maximum of the day when the accident occurs.
Pattern b : The absolute humidity is decreasing when the accident occurs.

not all the accidents occurred when the relative humidity reached its maximum on the day of the accident.

(3) When the daily absolute humidity changes for the 30 days preceding the accidents were examined, it was found that 27 of the 34 accidents occurred when the absolute humidity had been fairly constant at approximately 20 g·m^{-3} for more than ten days or when it had increased to around this value at the time of the accident. In addition, an examination of the absolute humidity changes in the 24 hours preceding the accidents indicated that for 12 of the 16 accidents analyzed, the absolute humidity had either been approximately constant at 20 g·m^{-3} or increased to this value during the 24 hours preceding the accident.

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硝酸エステルおよびその関連製品の自然発火事故と気象状況との関連性

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硝酸エステルおよびその関連製品の自然発火事故と気象状況の関連性を調査した。事故発生前30日間の日最高気温と日平均相対湿度を調査したところ，概ね30℃の日が10日間以上継続する場合，あるいは，徐々に気温が上昇し，事故発生日に概ね30℃に達する場合に事故が発生していることが分かった（収集した事故事例34件中25件）。一方，事故発生前24時間の気温および相対湿度の変化では，必ずしも気温および湿度が高い時間帯に事故が発生していないことが分かった。絶対湿度の事故発生前30日間の変化を調査したところ，絶対湿度が概ね20 g·m^{-3}の日が10日間以上継続する場合，あるいは，徐々に絶対湿度が上昇し，事故発生日に概ね20 g·m^{-3}に達する場合に事故が発生していることが分かった(34件中27件)。同様にして，事故発生前24時間の絶対湿度の変化を調査したところ，事故発生時間が分かる16件の事故のうち12件で事故発生時までに20 g·m^{-3}に絶対湿度が上昇していることが分かった。

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