What happens to hop pellets during unexpected warm phases?

Adrian Forster *

Introduction

Today, production and storage of hop products largely take place under defined conditions. Special care is taken that negative influences - such as the presence of oxygen and high temperatures - on the quality are kept to a minimum. Comprehensive documentation on this topic is available (1). On the other hand, there is still little or no interest - as regards transport conditions. Temperature records during long-lasting transportation to Asian and South American countries, however, give rise to further, more intensive investigation.

The problem of excessive temperatures, to which hop pellets are sometimes exposed, has already been discussed in a previous paper (2). These results can be supplemented by the following observations and investigations.

What happens in principle?

Firstly, some rules to degradation processes from the EBC-Manual "Hops and Hop Products" (1):

- *"Alpha-acids oxidise when they are exposed to air, but they also degrade in an inert atmosphere. Up to 50 % of the decrease of alpha-acids in an inert environment can be explained by the formation of iso-alpha-acids.*
- *Beta-acids oxidise in the presence of air similar to alpha-acids, but they remain stable in inert atmosphere at temperatures of up to 30°C.*
- *Hard resin components increase in the presence of air, but they remain stable in inert atmosphere. Hard resin components are therefore with good reason considered as oxidation products of bitter acids and defined as polar bitter substances."*

Furthermore, the following factors are important with regard to the ageing of pellets:

- *"In an inert atmosphere, low volatile components develop with high partial vapour pressure. A kind of "solvent smell" may result, especially at higher temperatures. These substances cause a pressure increase in a closed packaging, which even may cause the foil to burst.*
- *Pellets are generally more reactive than cone hops, which can be explained by the ground lupulin glands. The corroding surface increases due to the spread resins. Furthermore part of the protection against the diffusion of oxygen is lost due to the squashed lupulin membrane.*

The cold storage of pellets is consequently absolutely recommended."

The authors deduced from these facts the following:

"In order to avoid damage to hop pellets during transportation and storage the following 'rules' should be taken into account:

- *Warm conditions over 25 to 30°C should be avoided. The formation of gas within the pack, due to chemical reactions, can cause the foil to rupture. This inevitably leads to oxidation or even to the total spoilage of the pellets. Care should also be taken during the transport to avoid excessively high temperatures.*

* Dr.-Ing. Adrian Forster, Hopfenveredlung St. Johann

- *Breweries should make clear arrangements in order to avoid any warm periods of storage. Even a provisional storage of only a few weeks in warm atmosphere, for example in the harbour effects the quality."*

If a closed pellet foil is exposed to higher temperatures in excess of approx. 25°C, low volatile gases are formed in the foil and the volume increases correspondingly. This can cause a ballooning of the foil.
A summary of the above-mentioned points results in the following picture:

- Fig. 1 shows the reactions taking place in a tight foil, which is protected against oxygen:
  - alpha-acids decrease
  - iso-alpha acids are formed
  - beta-acids remain stable
  - the gas volume and consequently the pressure inside the foil increase.
- Fig. 2 shows the processes which take place in an open foil:
  - alpha and beta-acids decrease drastically in the presence of air oxygen
  - the atmospheric pressure cannot change.
- Fig. 3 shows a combination of the two above-mentioned cases (worst case):
  - Initially the foil is tight and the reactions depicted in fig. 1 take place.
  - However, the inside pressure increases in such a way that a leakage in the foil is caused, the gases escape and air penetrates. The processes depicted in fig. 2 take place.

If this combination occurs during a warm phase, for example during the transport on a ship, the hop pellets may become practically useless.

Recent observations regarding the balooning effect of foils

Already many years ago, an increase of low volatile aroma components during the inert storage of hop powder was noticed. This, however, was explained as a hop typical reaction (3). Surprisingly, the phenomenon of balooning also occurred with "side products" like lupulin-free coarse material or spent hops resulting from the production of lupulin-enriched pellets. Since these products consist of leaf and string parts of the hop cone, it becomes obvious that reactions take place, which are also possible with hop unspecific plant material .

In a subsequent step, the gases in the foils with pellets and spent hops of different varieties were investigated. The identification of the extremely low volatile components was performed at the "Lehrstuhl für Chemisch-Technische Analyse und Chemische Lebensmitteltechnologie" of Prof. Parlar in Weihenstephan by means of head space capillary gas chromatography combined with a mass spectrometer. Some of the identified components are listed in table 1. Only a few of them are typical to hops. Sensorily, the impression between solvent (acetone) and herblike (dimethyl sulphide and dimethyl disulphide) resulted.

Possible reasons are for example thermal reactions, as known from the degradation of amino acids (Strecker degradation). However, since some of the listed components may also be reaction products of anaerobic micro-organisms, investigations were made in this direction as well.
At first, the micro-biological condition of some samples of pellets and spent hops were examined. The typical result is shown in table 2. In the present case, only facultative anaerobics such as entero bacteria can form the reaction products. Samples, which were subject to temperatures of 35 or 50°C for 7 days, however, mostly lost their micro-biological trimming (table 3). Since gases were also formed at temperatures over 50°C, doubts arose on the micro-biological theory.

To test this theory, samples of hops and spent hops were sterilized in a special procedure at 85°C. Table 4 demonstrates the success of such a treatment. When these sterile samples were subject to a subsequent warm phase in a gas tight foil, the same gas formation occurred as in the untreated samples. Therefore, it seems unlikely that facultative anaerobics essentially contribute to the formation of low volatile components.
Consequently, the following points can be listed as reasons for the balooning of pellet foils at higher temperatures:

- Desorption of the inert gas used in the packaging
- Desporption of low volatile hop aroma components
- Formation of low volatile components due to chemical reactions of bitter substances and especially
- Formation of low volatile components from thermal reactions of organic substances.

Warm phases during transportation

The following examples of warm phases during the transportation are possible:

- Land transportation in summer lasting several days. For example, a truck standing in the sun during the weekend or lengthy rail transportation.
- Overseas transportation on container ships
- Intermediate storage in harbours or unprotected halls.

During the last years we have been attaching temperature loggers to every overseas container. From the time of loading in the pellet plant until unloading in the brewery the temperature was registered in intervals of 10 to 30 minutes. The figures 4 to 7 are examples of temperature records with the following characteristics:

- Figure 4: Loading from the cold storage in winter, transport by ship, at the beginning still cold, max. temperatures below 25°C, arrival in Japan in winter. This curved form can be regarded as most satisfactory.
- Figure 5: Loading from the cold storage in summer with a quick temperature rise already occurring on land, reaching a max. temperature of over 30°C around Singapore, upon arrival in the Far East standing several days at the port of destination (alternation of day and night temperatures).
- Figure 6: Loading from the cold storage in summer (see fig. 5), the container is on deck and thus exposed to alterations in temperature between day and night (temperatures between 30 and 50°C).
- Figure 7: Loading from the cold storage in autumn, the container is near a source of heat (heated oil tanks) on the ship and reaches peak temperatures of around 50°C. This curved form is especially unfavourable.

From previous experience, we have deduced the following rating:

- Max. temperature below 25°C: good
- Max. temperature 25 – 30°C: acceptable at < 5 days
- Max. temperature 30 – 35°C: acceptable at < 2 days
- Max. temperature 35 – 40°C: dangerous
- Max. temperature over 40°C: unacceptable

The conclusion is that damaging of the products can be nearly avoided only by shipping in winter at low starting temperatures. In the critical season (April to October) excessive temperatures cannot be ruled out.

Modern container ships increase the above-mentioned problems. The instructions regarding the position of the container (e.g. “store below the water line”, “store away from boilers and heated tanks” or “store on deck protected from the sun”) are not observed. The containers below deck are no longer ventilated due to cost reasons. The decks are open to reduce construction costs. The ships are driven by heavy oil, which – for liquefying purposes - is stored in tanks at temperatures up to 80°C. Containers are therefore often placed between two sources of heat (sun on deck, heat in the ship).
The problem of excessive temperatures can thus only be avoided by shipping in the winter season or in reefer containers, where the requested temperatures are guaranteed. Freight for reefer containers, however, costs more than double the price. In many cases, however, these additional costs are compensated alone by the fact that alpha-acids are maintained during transportation. In table 5, from more than 200 records the average alpha-acid losses during an overseas transportation were listed in relationship to the temperature conditions. According to the variety and the market price, a cold transport is justified not only for quality but also for economic reasons.

Summary

Whereas much importance is attached to a quality maintaining production and storage of hop pellets, less attention is often paid to the transportation to the brewery. However, the often prevailing temperatures in excess of 25°C may cause considerable damage, since chemical reactions take place even in an air-protected foil. Besides the degradation of alpha-acids, low volatile components are formed. Surprisingly, these processes also take place in hop plant material untypical to hops. In the worst case, the pellet foil expands in such a way that a leakage is inevitably caused and the contents of the foil oxidise completely due to the penetrating air.
Trials proved that a possible attack of micro-organisms cannot be responsible for the formation of these extremely low volatile components. Probably, thermal reactions like a “Strecker”-degradation of amino acids take place. The substance mixture can sensorily be described as solvent and/or herblike.
In the case of overseas transports in winter, peaks of temperatures between 20 and 25°C are prevailing in the most favourable cases, whereas during summer shipment temperatures up to 50°C occur. It is obvious that hop pellets are damaged under these conditions. The best solution of the problem in critical seasons is only the shipment in reefer containers. Although the freight costs increase by more than the double, these additional costs are compensated by the maintenance of alpha-acids.

Literature:

1) Benitez J. L., Forster A., De Keukeleire D., Moir M., Sharpe F. R., Verhagen L. C., Westwood K. T.: EBC-Manual of Good Practice: Hops and Hop Products Hans Carl-Verlag, Nürnberg, 1997, ISBN 3-418-00758-9.

2) Forster A.: Brauerei- und Getränkerundschau , 107, Nr. 10, 231 - 237, (1996)

3) Narziss L. and Forster A.: Brauwiss. Jg. 25, S. 8-16 (1. 1972) and 45-50 (2. 1972)

Expression of thanks:

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Table 1: Identified Components from the Gas Volume of Hops and Spent Hops (in the order of retention times)

Components	
CO_2	2-Methyl butanal
2-Methyl-2-buten	3-Methyl butanal
Isoprene	2-Ethyl furan
CS_2	4-Methyl-2-pentanon
Dimethyl sulphide	Methyl-3-methyl butanoat
Propanal	2-Methyl-3-buten-2-ol
Acetone	Dimethyl disulphide
Methyl furan	2-Methyl butanol
	2-Pentyl furan

Table 2: Typical Attack of Micro-Organisms on Hop Pellets (number per gram)

Total number of germs	10^2 to 10^6
Pseudomonas aeruginosa	n.d..
Staphylococcus aureus	n.d.
Escherichia coli	n.d.
Salmonellas	n.d.
Entero bacteria*	n.d. to 10^5
Yeasts	n.d. to 10^3
Mould	n.d. to 10^2

**) facultative anaerob*

Table 3: Micro-Biological Attack after 7 days' Storage at 2 Temperatures (number per gram)

		Initially	35°C	50°C
Sample 1:	Total number of germs	8.8×10^4	3.0×10^2	n.d.
	Entero bacteria	6.0×10^4	$< 10^2$	n.d.
Sample 2:	Total number of germs	1.0×10^5	7.0×10^2	1.0×10^2
	Entero bacteria	3.6×10^3	$< 10^2$	n.d.
	Yeasts	6.0×10^2	n.d.	n.d.
	Mould	3.0×10^2	n.d.	n.d.
Sample 3:	Total number of germs	6.0×10^5	3.0×10^3	n.d.
	Entero bacteria	10^4	n.d.	n.d.
	Yeasts	3.0×10^2	n.d.	n.d.
	Mould	2.4×10^3	n.d.	n.d.

Table 4: Micro-Biological Attack before and after the Sterilization at 85 °C (number per gram)

	Initially	after sterilization
Total number of germs	1.5×10^5	n.d.
Entero bacteria	4.0×10^3	n.d.
Yeasts	1.4×10^3	n.d.
Mould	4.0×10^2	n.d.

Table 5: Alpha-Acid Losses during an Overseas Transportation in % relative

Shipping temperatures	alpha losses in % relative
up to 25 °C	3 to 6
up to 30 °C	5 to 8
up to 35 °C	6 to 10
over 35 °C	up to 15

Figure 1: Principal Processes during the Storage of Pellets (> 25 °C)
Inert atmosphere = gas flushed, closed, diffusion tight foil

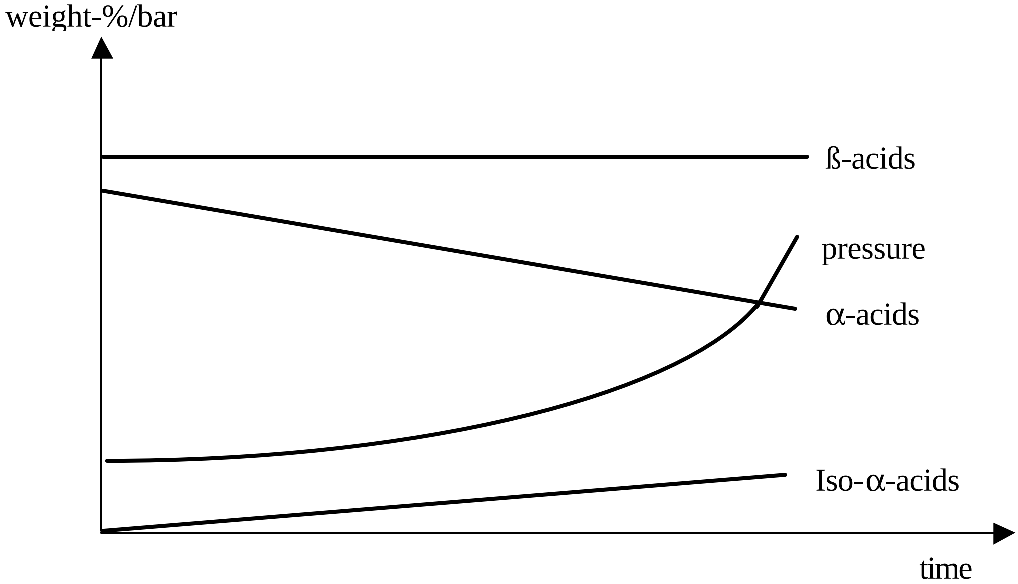

Figure 2: Principal Processes during the Storage of Pellets (> 25 °C)
Open foil, in the presence of air oxygen (Iso-α-acids not detected)

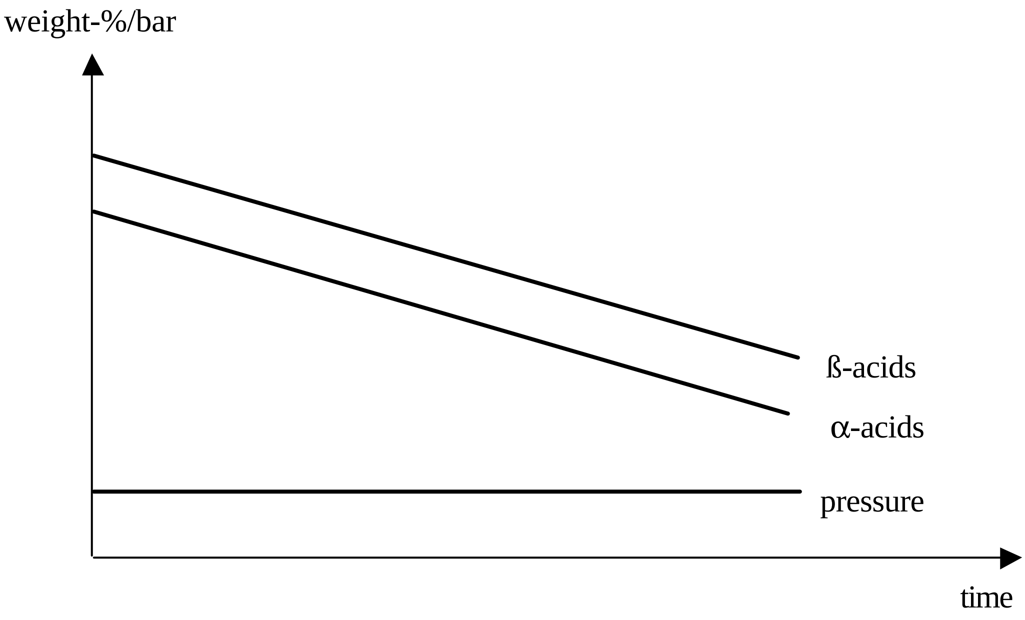

Figure 3: Combination of the 2 Phenomenons: Initially Inert Atmosphere, Later Reactions in the Presence of Air Oxygen

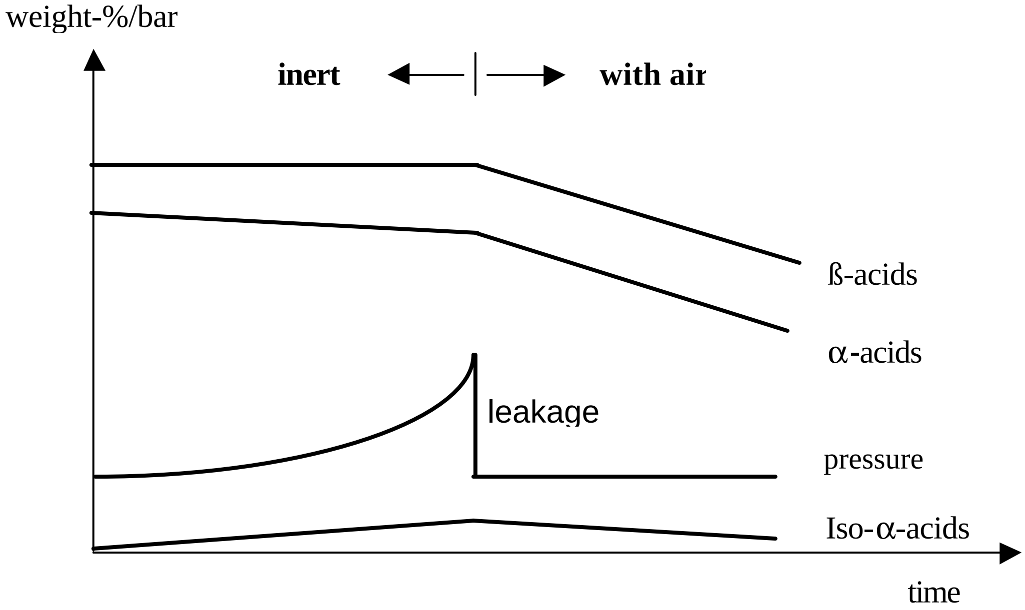

Figure 4: Temperature Graph in a Container Shipped to Far East – "Favourable"

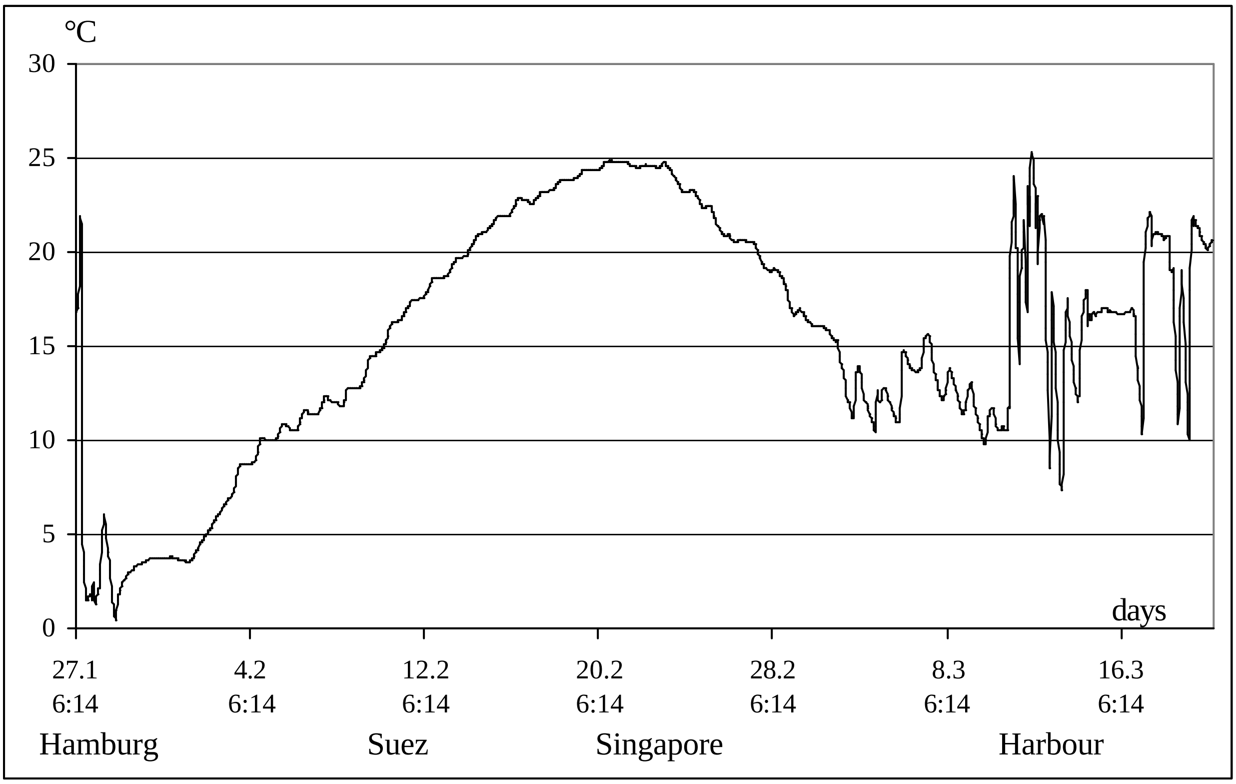

Figure 5: Temperature Graph in a Container Shipped to Far East - "Problem in the Harbour"

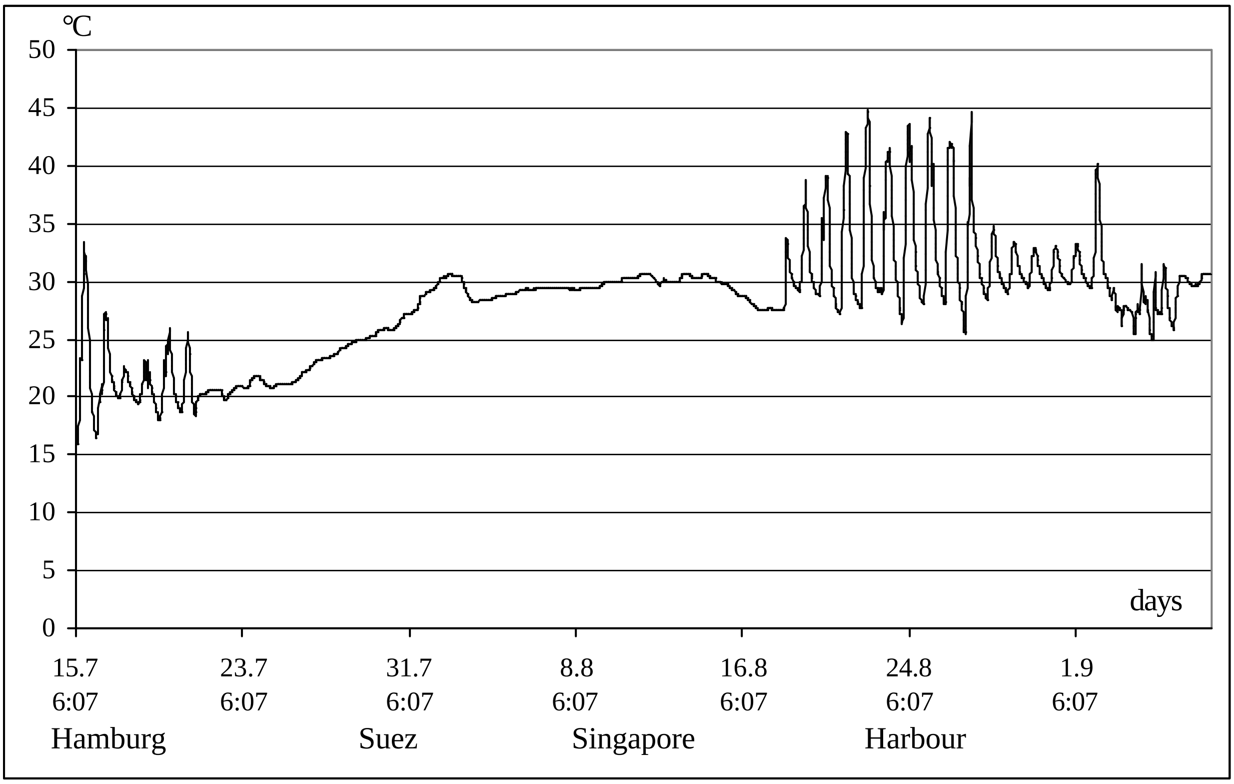

Figure 6: Temperature Graph in a Container Shipped to Far East – "Problem on Deck"

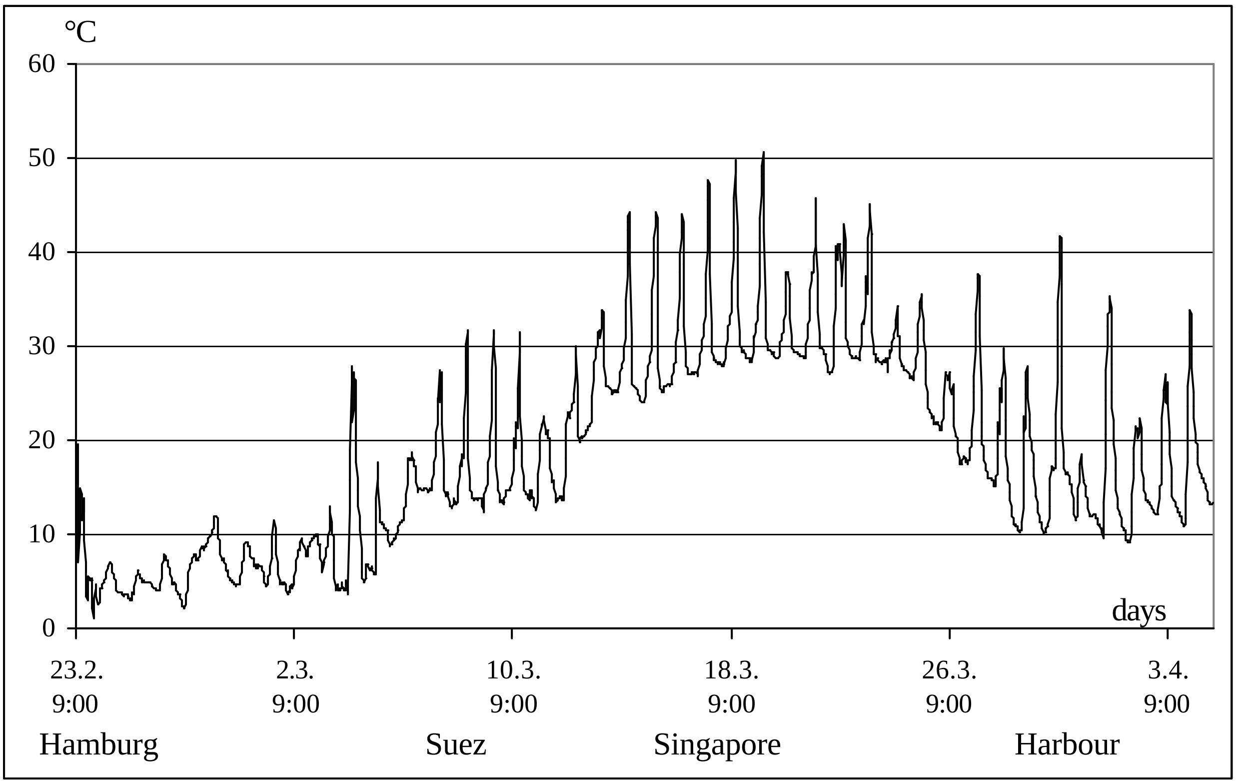

Figure 7: Temperature Graph in a Container Shipped to Far East – "Problem in the Belly of the Ship"