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NATIONAL STANDARD

OF THE PEOPLE'S REPUBLIC OF CHINA

GB/T 21902-2008

Emission standard of pollutions for synthetic leather and artificial leather industry

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Issued on: June 25, 2008 Implemented on: August 01, 2008

Issued by: General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China;

Environmental Protection Ministry of the People's Republic of China.

Public Notice by Environmental Protection Ministry of the People's Republic of China

No.26, 2008

To prevent pollution, improve the environment and protect human health in accordance with "Environmental Protection Law of the People's Republic of China", "Water Pollution Control Act of the People's Republic of China" and "Prevention and Control of Air Pollution of the People's Republic of China", now the 11 standards such as "Emission Standard of Water Pollution for Pulping and Papermaking Industry" are approved as the emission standard of state pollution emission. They are jointly issued by State Administration for Quality Supervision and Inspection and Quarantine) and Environmental Protection Ministry.

Standard names and numbers are as follows:

- 1. Emission standard of water pollution for pulping and papermaking industry (GB 3544-2008)
- 2. Emission standard of electroplating pollution (GB 21900-2008)
- 3. Emission standard of water pollution for feather industry (GB 21901-2008)
- 4. Emission standard of water pollution for synthetic leather and artificial leather industry (GB 21902-2008)
- 5. Emission standard of water pollution for fermented pharmaceutical industry (GB 21903-2008)
- 6. Emission standard of water pollution for chemical complex pharmaceutical industry (GB 21904-2008)
- 7. Emission standard of water pollution for extracted pharmaceutical industry (GB 21905-2008)
- 8. Emission standard of water pollution for Chinese medicine pharmaceutical industry (GB 21906-2008)
- 9. Emission standard of water pollution for biological engineering pharmaceutical industry (GB 21907-2008)
- 10. Emission standard of water pollution for mixed pharmaceutical industry (GB 21908-2008)
- 11. Emission standard of water pollution for sugar industry (GB 21909-2008)

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In accordance with relevant laws and regulations, the standards above are mandatory.

The standards above shall be implemented since August 1st 2008.

The standards above are published by China Environment Science Public Press. The contents of the standards may be searched from the website of Environment Protection Department (hz.mcp.gov.cn).

Since the implementation day, "Emission Standard of Water Pollution for Papermaking Industry" (GB 3544-2001) shall be abolished.

Notice is hereby announced.

June 25th 2008

Public Notice by Environmental Protection Ministry of the People's Republic of China

No.28, 2008

To protect environment and prevent pollution, it is studied and decided that the water pollutants special emission limit (hereinafter referred to as emission limit) of state emission standard in Taihu Lake Basin will be carried out since September 1st 2009 and the standard names are as follows:

- 1. Emission standard of water pollution for pulping and papermaking industry (GB 3544-2008)
- 2. Emission standard of electroplating pollution (GB 21900-2008)
- 3. Emission standard of water pollution for feather industry (GB 21901-2008)
- 4. Emission standard of water pollution for synthetic leather and artificial leather industry (GB 21902-2008)
- 5. Emission standard of water pollution for fermented pharmaceutical industry (GB 21903-2008)
- 6. Emission standard of water pollution for chemical complex pharmaceutical industry (GB 21904-2008)
- 7. Emission standard of water pollution for extracted pharmaceutical industry (GB 21905-2008)
- 8. Emission standard of water pollution for Chinese medicine pharmaceutical industry (GB 21906-2008)
- 9. Emission standard of water pollution for biological engineering pharmaceutical industry (GB 21907-2008)
- 10. Emission standard of water pollution for mixed pharmaceutical industry (GB 21908-2008)
- 11. Emission standard of water pollution for sugar industry (GB 21909-2008)
- 12. Control standard of pollution for municipal solid waste landfill (GB16889-2008)
- 13. Emission standard of water pollution for heterocyclic pesticide industry (GB21523-2008)

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Specific administrative region Scope for special emission limit in Taihu Lake Basin would be announced separately.

Notice is hereby given.

July 2nd 2008

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Foreword

This Standard is regulated to protect environment, prevent pollution and improve industrial production technology and pollution treatment technology of synthetic leather and artificial leather in accordance with Environmental Protection Law of the People's Republic of China", "Water Pollution Control Act of the People's Republic of China", "Air Pollution Control Act of the People's Republic of China", "Marine Environment Protection of the People's Republic of China", and "Decision on implementing the scientific development of the State Council to Enhance Environmental Protection".

The standard specifies the emission limit and monitoring requirements of water and air pollution for synthetic leather and artificial leather. Special emission limit of water pollutants is specified in this Standard to enhance the harmonious development of region economy and environment, drive the adjustment of economic structure and change in the pattern of economic growth and guide the development direction of industrial production technology and pollution treatment technology.

Pollution emission concentration of this Standard acts as quality concentration.

Stink pollution emission and environmental noise of synthetic leather and artificial leather enterprises apply the related emission standard of state pollution and their identification, treatment and disposition of solid waste apply the control standard of state solid pollution.

This Standard is issued for the first time.

Since the implementation day of this Standard, the emission control of water and air pollution of synthetic leather and artificial leather enterprises would be formulated and carried out according to this Standard and the related regulations in "Integrated Waste-water Emission Standard" (GB 8978-1996) and "Integrated Air Pollution Emission Standard" (GB 16297-1996).

This Standard is formulated by Science Standard Department of Environment Protection Ministry.

The main drafting departments of this Standard are as follows: Wenzhou City Environment Monitoring Center Station, Wenzhou City Environment Protection and Design Academy of Science, Wenzhou Artificial Leather Co., Ltd and Environment Standard Research Academy of Ministry of Environmental Protection.

And it is approved by Ministry of Environment Protection on May 29th 2008.

This Standard would be carried out since August 1st 2008.

Pollution Emission Standard of Synthetic Leather and Artificial Leather Industry

1. Scope

This Standard specifies water and air pollution emission limit of characteristic production technology and equipment for synthetic leather and artificial leather industry enterprises.

This Standard is applicable to environmental impact assessment, environment protection facilities design, environment protection acceptance, and water and air pollution emission management of construction project for available synthetic leather and artificial leather industry.

This Standard is applicable to pollution emission behavior allowed by laws. The site selection of pollution sources newly established and the management of existed pollution sources in special protection area shall be carried out in accordance with related provisions of the laws, regulations and rules such as "Atmospheric Pollution Prevention Law of the People's Republic of China", "Water Pollution Control Act of the People's Republic of China", "Solid Waste Pollution Control Act of the People's Republic of China", "Radioactive Pollution Control Act of the People's Republic of China", and "Laws on Environment Impact Assessment of the People's Republic of China".

Water pollutants emission control requirements of this Standard is applicable to enterprises for emission behavior of environmental water.

When the enterprises discharge waste-water to city drainage system equipped with sewage treatment plant, the pollution emission control requirements shall be decided by enterprises and city sewage treatment plant according to its processing capacities or related standard, and be reported to local environment protection competent department for reference. City sewage plant shall ensure that the emission pollution meeting the related emission standard's requirements.

When construction project plans to discharge waste-water to city drainage system equipped with sewage treatment plant, it shall be carried out by construction organization and city sewage plant according to the regulations of preceding clause.

2. Normative references

This Standard quotes the following documents or their provisions.

GB/T6920-1986 Water quality pH measure glass electrode method

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GB/T7478-1987 Water quality ammonium measure distillation and titration

GB/T7479-1987 Water quality ammonium measure Nesster's reagent colorimetric method

GB/T7481-1987 Water quality ammonium measure salicylic acid spectrophotometric method

GB/T11890-1989 Water quality benzene series measure gas chromatographic method

GB/T11893-1989 Water quality total phosphorus measure ammonium molybdate spectrophotometric method

GB/T11894-1989 Water quality total phosphorus measure alkaline potassium persulfate decomposes ultraviolet spectrophotomety

GB/T11901-1989 Water quality suspended solids measure gravimetric method

GB/T11903-1989 Water quality chromacity measure

GB/T11914-1989 Water quality measure of chemical oxygen demand (cod) dichromate titration

GB/T16758-1997 Classification and technical specifications of exhaust hood

GB/T16157-1996 Particulate substance measure of solid pollution source exhaust and sampling method of gaseous pollutant

GB/T160.62-2004 Toxic air substance measure in workplace amide compounds

GB/T160.55-2004 Toxic air substance measure in workplace aliphatic series ketone compounds

GB/T160.42-2007 Toxic air substance measure in workplace aroma hydrocarbon compound

HJ/T195-2005 Water quality ammonia nitrogen measure gaseous phase molecular absorption spectroscopy

HJ/T199-2005 Water quality total nitrogen measure gaseous phase molecular absorption spectroscopy

HJ/T399-2007 Water quality measure of chemical oxygen demand (cod) rapid decomposition spectrophotometric method

"Automatic Monitoring and Management Method of Pollution Sources" (No.28 Order of State Environmental Protection Administration)

- **4.2.5** It is necessary to set up partial or overall gas collection system and concentrated purification treatment device for production technology and facilities which generate air pollution. The purified gas is discharged through exhaust funnel. Annex A may be for the reference for the setting of collection system.
- **4.2.6** The height of all the exhaust funnels shall not be less than 15m and be 3m higher than building in a 200m radius. All the exhaust funnels which do not meet this requirements shall be 50% stricter than the emission limit.

4.3 Other control requirements

4.3.1 Waste-water treatment devices, waste-gas collection devices and treatment devices shall be operated according to the designed and adjusted parameter conditions.

For the gas treatment system of DMF treatment devices which adopt water-washing recovery mode, the DMF mass fraction of recycling liquid shall not be less than 10%, unless it meets the designed and adjusted parameter requirements with the confirmation of technical document and operation record.

- **4.3.2** Container contained with VOCs shall be covered with sealing cover.
- **4.3.3** When waste-water treatment devices, waste-gas collection facilities, or treatment devices are operating, the enterprises shall record the main parameters.

Example [1] of record requirements: Gas treatment system adopts water-washing recycling and treatment devices. The main parameters include recycling liquid concentration and amount, washing recycling water quantity of all washing tank, recycling water temperature, processed gas volume (or fan revolving speed), and operation time.

Example [2] of record requirements: Gas treatment system adopts condensation recycling and treatment devices. The main parameters include recycling liquid amount, processed gas volume (or fan revolving speed), operation time, and inlet temperature and outlet temperature of condensation liquid.

- **4.3.4** Dust generated by dosing, buffing and polishing and particulate substance generated in other technological process shall be collected and treated with appropriate dust removal devices.
- **4.3.5** Production facilities shall be processed with reasonable venting practice. It must not be diluted and discharged at will. Before there is standard gas discharge of unit-product regulated by the state, the measured concentration is temporarily regarded as the basis of meeting the standard's requirements.

5. Pollutants monitoring requirements

A.3.2.3 Measurement point of control wind speed for half-sealed hood is at the central position of exhaust hood's mouth.

If applicable, measurement point of control wind speed for half-sealed hood is at the central position of exhaust hood's mouth.

The measurement points of open-type exhaust hood are respectively located within the scope of 5cm surrounding the working position (or at the extended edge) where is the farthest from the exhaust hood's mouth, at every directions. It is measured at the position where has the biggest wind speed. Measured results at the working position where is the farthest from the exhaust hood mouth side, at every directions, shall all meet the technical requirements in the tables of this Standard.

- A.3.2.4 While measuring, please not be disturbed by external ventilation. If necessary, exhaust fan and window shall be closed.
- A.3.2.5 If measuring number is unstable, average value of 1 min may be taken.
- A.3.3 Indirect method such as measuring ventilation air volume may be adopted to measure the control wind speed. Compare the corresponding design parameters or re-calculate the control wind speed.

A.4 Evaluation of collection conditions

- A.4.1 VOCs mass concentration dissipating from monitoring position
- A.4.1.1 Monitoring method shall be adopted to measure dissipated VOCs mass concentration.

A.4.1.2 Monitoring position

While the material dissipating VOCs is in open type, it shall select the monitoring position at 10cm from the material surface. While material dissipating VOCs is in half-closed type, it shall select the monitoring position at 10cm from the inner-mouth surface. If this position is less than 10cm distance from material surface or the width of mouth surface is less than 10cm, mouth surface shall be chosen.

The distribution of monitoring position on the surface of monitoring position shall be representative, and shall include at least two positions with the densest anticipated VOCs concentration.

- A.4.1.3 While monitoring, production facilities shall discharge the product with the biggest concentration during the production forecast period, and produce normally and continually.
- A.4.1.4 VOCs mass concentration shall be measured according to the method in Annex C. VOCs mass concentration refers to the sum of all organic pollutant concentration. While

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R — Recovery rate obtained from recovery test. Dimension is 1.

C.4.4.2 Instrument direct determination sampling method

Please refer to the sampling methods of 9.2.2 and 9.4.3 in GB/T 16157-1996.

Procedures

Set up appropriate operation conditions for gas chromatography.

Connect sampling system. Make sure all connector to be tight. Open heating device of sampling tube and sampling connector to make the temperature to be more than 110°C. Conduct 3-point calibration. Set up standard curve. After all samples are analyzed, re-conduct the medium level calibration das analysis for each organic substance. If relative deviation of response coefficient for each organic substance before-analysis and after-analysis is not more than 5%, then it may directly use the before-analysis standard curve; if relative deviation is more than 5%, then it is necessary to analyze standard gas with other concentrations, and adopt the joint standard curve that is confirmed and calibrated before-analysis and after-analysis.

The end of sampling tube is placed at the center of emission pipe. Extract the gas. After completely washing the sampling tube, connecting pipe and quantification pipe, use the conditions while calibrating to inject sample for analysis. Use calibration curve to calculate. Others may refer to air pocket sampling method.

C.4.4.3 Adsorption tube sampling method

Any adsorbent that meets the recovery test requirements may be used. Main interference of some adsorbent is vapor. If there exists some vapor interference, a small ice-bath striking moisture collector may be added in front of adsorption tube. Water collected from moisture collector shall be analyzed at the same time. Recovery tests shall be made for both moisture collector and adsorption tube. The sum of recoveries shall meet the requirements.

C.4.4.3.1 Sampling

Refer the sampling method of 9.4.1 in GB/T 16157-1996.

Notes: Mass concentration and sampling volume of waste-gas shall be estimated before sampling, so as to avoid adsorption penetration (if relative humidity of sample gas is more than 2%~3%, adsorption amount of adsorption pipe will drop sharply).

C.4.4.3.2 Sample analysis

C.4.4.3.2.1 Calibration

Gas chromatograph shall be operated according to the instrument's instructions. The established optimization condition shall be documented, so as to make sure all operations to be conducted under this optimization condition.

If thermal desorption is used, gas standard shall be prepared according to C.4.4.1.2. If solvent desorption is used, liquid standard in desorption thermal shall be prepared. At least 3 different standards shall be used, and select appropriate mass concentration.

C.4.4.3.2.2 Analyze sample according to the calibrated conditions

C.4.4.3.3 Calculation

Mass concentration of each organic substance under standard state is calculated by Formula (C.3).

$$\rho_{\rm C} = \frac{m}{V_{\rm nd}R} \tag{C.3}$$

Where:

ρ_c — mass concentration of organic substance of dry air under standard state, mg/m³;

m — the mass of organic substance in adsorption tube (including moisture collector) obtained from standard curve, μg ;

V_{nd} — dry-gas volume under standard state, L;

R — Recovery rate obtained from recovery test. Dimension is 1.

C.4.5 Quality control and quality assurance

C.4.5.1 Recovery test

After all related pollutants being predicted and identified, appropriate recovery test shall be made for sampling system of related pollutants.

C.4.5.1.1 Recovery test of air pocket sampling

Generally, after analyzing 3 samples, an air pocket sample is selected as the sample for spiked recovery test. Paste a label on it. Mixture (gaseous state or liquid state) containing all target organics is added into air pocket. Theoretically, spiked concentration shall be 40%~60% of average of 3 measured air pocket samples; it some target compound in air pocket sample is not detected, spiked amount shall be 5 times of detection limit of this compound. After the storage time is same as the on-site sample air pocket, analyze the spiked air pocket for 3 times. Average recovery rate (R) of each spiked substance is calculated by Formula (C.4).

$$R = \frac{t - u}{s} \tag{C.4}$$

Where:

R — average recovery rate. Dimension is 1;

t — total mass concentration measure after spiking, mg/m³;

u — measured mass concentration without spiking, mg/m³;

s — spiked theoretical mass concentration, mg/m³.

Effective range of average recovery rate is: 0.70<R<1.30. if R value can not meet the requirements, this sampling technology is not applicable.

C.4.5.1.2 Recovery test of instrument direct test sampling

After calibration procedures, use a kind of standard gas in medium mass concentration level, in which it contains at least one kind of standard gas of target compound, to respectively add to the inlet (or the close position as much as possible, but it must be before filtering material) of sampling tube and the inlet of analytical instrument. Repeat the test for 3 times. The difference BETWEEN the average response value of standard gas passing through sampling tube inlet AND the average response value going directly into the instrument analysis shall be within 10%. If the difference is more than 10%, it shall thoroughly check the leakage; re-analyze the standard gas that passes through sampling system; until it complies with the standard.

C.4.5.1.3 Recovery test of adsorption tube sampling

Recovery study is conducted on the sampling site according to sampling method of the adsorption pipe. Two same-sets of sampling devices are used; one set is spiking; the other set is without spiking. Two sampling tubes are in parallel in the smoke flue, at the distance of 2.5cm, on the same section. All expected compounds (gaseous state or liquid state) are added in adsorption pipe of spiking device before sampling. Spiking amount shall be 40%~60% of collection amount of un-spiking devices. Two sets of devices collect the pipe gas at the same time. Same-instrument and same-method are used to analyze the adsorption pipe samples collected by two sets of devices. Repeat the test for 3 times. Average recovery rate (R) of each spiking substance is calculated by Formula (C.5).

$$R = \frac{(t-u) \times V_s}{S} \tag{C.5}$$

Where:

R — average recovery rate. Dimension is 1;

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solution is to thoroughly wash GC sample injector while analyzing different types of samples.

- C.4.7.4 When sample contains water vapor, it is necessary to measure water vapor content and revise the mass concentration of gas-state organic substance.
- C.4.7.5 Analytical time of gas chromatograph of each sample shall be long enough to make sure that all peaks are eluted.

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