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The Properties and Development of Sulfur-Free Odorant for Town Gas

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Abstract: In this paper, the characteristics, advantages and disadvantages of natural gas sulfur-free odorants and traditional sulfide odorants, as well as the application examples of sulfur-free odorants at home and abroad are analyzed and compared, and the differences between the two odorants in natural gas treatment are discussed. The research shows that the natural gas sulfur-free odorant has the advantages of being more environmentally friendly, safer and more economical than the traditional sulfide odorant. Combined with the actual application cases, the future development trend and prospect of sulfur-free odorant in the natural gas industry are prospected.

Keywords: Natural gas odorization; sulphur-free odorant; traditional sulfide odorant; future development.

1. Introduction

As an important energy resource, natural gas plays an important role in the energy structure of the world today. Natural gas is mainly composed of methane (CH4), which also contains some other hydrocarbons, such as ethane, propane and butane [1]. Natural gas is almost free of sulfur, dust and other harmful substances. It is non-toxic and easy to emit. The carbon dioxide produced during combustion is less than other fossil fuels, which has little effect on the greenhouse effect of the environment. It is a clean energy, and the price is economical. It is not easy to accumulate into explosive gas after leakage, which is relatively safe. Natural gas plays an important role in the energy field. It not only occupies an increasing proportion in the energy consumption structure, but also plays a key role in promoting energy cleanliness, ensuring energy security and promoting economic development.

With the increasing demand for clean energy in China, the status of natural gas is expected to be further enhanced in the future. However, while natural gas brings convenience to residents ' life, industrial production and commercial activities, there are also many safety hazards. Natural gas itself is a colorless and odorless gas, which is difficult to be intuitively detected when it leaks. Therefore, in order to improve the safety of natural gas and ensure the safety of people 's lives and property, a small amount of chemical substances containing irritating odor are usually added to natural gas as a odorant, so that it can be detected when it leaks, so that it can be repaired and processed in time to avoid accidents.

At present, most of the odorants widely used in the world are tetrahydrothiophene (THT) or thiol compounds (RSH). Among them, the application time of thiol odorants is the longest, and the use range of THT is the widest. With the enhancement of people 's awareness of environmental protection and the expansion of the natural gas market, there are higher requirements for the control of sulfur content in natural gas. Because the components of the above two odorants contain sulfur (S) elements, they will produce harmful by-products such as sulfur dioxide during combustion, causing environmental pollution. At the same time, it will also have a certain impact on the product quality of some industrial customers. The research work of sulfur-free odorant will become the development trend of gas industry in the future [2].

2. Section Headings

At present, there are mainly three kinds of commonly used odorants, including thiols (such as ethanethiol, tert-butyl mercaptan, isopropyl mercaptan, etc.) and tetrahydrothiophene (cyclic sulfide) in traditional sulfide odorants and sulfur-free sulfur-free odorants without sulfur.

The price of thiol odorant is relatively low. Generally speaking, it is a colorless, odorous and volatile oily body. It has a strong odor and can effectively odorize, but it is easy to oxidize and unstable, and has certain pollution to the environment.

THT is an organic sulfur compound. Its pure substance is a colorless or yellowish transparent volatile liquid. It is insoluble in water and soluble in ethanol, ether, benzene, acetone, etc. It has good stability and oxidation resistance. The odor effect is good, the pollution to the environment is relatively small, but the cost is high [4].

Sulfur-free odorant is a colorless transparent liquid with a strong irritating odor. It is a mixture of 37.4%$C_4H_6O_2$(methyl acrylate),60%$C_5H_8O_2$(ethyl acrylate), 2.5%$C_7H_{10}N_2$(3-ethyl-2-methylpyrazine) and 0.1%$C_{15}H_{24}O$ (2,6-di-tert-butyl-4-methylphenol) [5].Sulfur-free odorants have less pollution to the environment and meet the requirements of environmental protection, but some sulfur-free odorants have low odor intensity and may need to be used in combination.

The physical and chemical properties of four common odorants are listed in Table 1-1.

In this paper, the characteristics of the most commonly used THT and emerging sulfur-free odorants at home and abroad and their application effects in practical engineering are compared and analyzed.

Table 1-1. Physicochemical properties of common odorants

category	tert-butyl thiols	ethyl mercaptan	thiophane	sulphur-free odorant
for short	TBM	EM	THT	S-Free
The main component molecular formula	$C_4H_{10}S$	C_2H_5SH	C_4H_8S	$C_4H_6O_2$、$C_5H_8O_2$
character	no color liquid	no color liquid	no color liquid	no color liquid
boiling point (℃)	64.3	35.1	121.0	80
solidifying point (℃)	-0.5	-147.8	-96.1	-72.0
flash point (℃)	-24	-45	19	5
ignition point (℃)	304	304	202	395
Density (20℃,g/cm^3)	0.7943	0.8315	0.9987	0.933
explosion limit (%)	2.8-18.0	2.8-18.2	1.1-12.1	1.6-23
water solubility	slightly soluble in water	slightly soluble in water	heteroalbumose	heteroalbumose

3. Factors Affecting the Conversion of Sulfur-free Odorants

In order to use sulfur-free odorant instead of traditional THT, the following main factors need to be considered in the natural gas pipeline network :

(1) Odor intensity and perception difference

The main function of gas odorant is to enhance the odor of specific gases in natural gas or other gas, so that it can be quickly detected when the gas leaks. Therefore, the odorant needs to have sufficient odor intensity to meet the threshold that can be detected by users when the gas leaks. The odor of THT is often described as a pungent odor similar to that of rubber or gasoline. Its odor is strong and persistent, and can be easily detected even at low concentrations, and the olfactory threshold of THT is relatively low, which means that people can notice its odor very early in the leak. Sulfur-free odorants have different odor characteristics. Their odors are usually described as odors similar to rotten eggs or sulfur. This odor is usually obvious, and its olfactory threshold is also low. It can also be detected at low concentrations.

(2) Chemical stability and reactivity

Under normal conditions, the sulfur-free odorant is relatively stable, does not react with the pipe, and has strong adaptability and no corrosion to various pipes. However, it may decompose at high temperature, high humidity or in the presence of catalysts, and it is easy to cause polymerization under the contact of sunlight, ultraviolet light, X-ray, etc., which means that under specific environmental conditions, sulfur-free odorants may lose their odorization efficiency or generate additional gases, which may affect the safety of the pipeline network. In contrast, THT has relatively good stability in natural gas.

(3) Toxicity and environmental impact

Traditional sulfide odorants (such as THT) usually use sulfides such as hydrogen sulfide as raw materials [6], which have obvious odorizing effect and can play a role quickly and effectively. However, sulfides have certain toxicity and corrosivity, and there are safety risks in the production and use process, which have potential hazards to the environment and human health. High concentrations of THT can cause discomfort to the human body, such as headache, eye irritation, etc. Long-term exposure to high concentrations of THT may have adverse effects on health. For the environment, THT has poor biodegradability and may stay in the environment for a long time, and will produce sulfide during use, thus affecting the ecosystem. Sulfur-free odorants usually use organic compounds as raw materials. Compared with traditional sulfide odorants, sulfur-free odorants do not contain sulfur elements, and their toxicity is usually lower than that of traditional sulfide odorants. In the process of production and use, the safety risk is also reduced, and the sulfur-free odorants are more easily degraded in the environment, and will not produce sulfide emissions during use, reducing the risk of pollution to the atmosphere and water sources, which is conducive to sustainable development.

(4) Compatibility and diffusion ability

The sulfur-free odorant should have good compatibility with natural gas and will not react with other components in natural gas to produce adverse chemical complexes. At the same time, compared with THT, the sulfur-free odorant has a stronger mixing ability with natural gas, and the diffusion in natural gas is faster and more uniform, effectively transmitting the leakage warning.

(5) Cost-benefit analysis

At present, most of the THT added by domestic gas companies rely on imports. Since 2020, due to the impact of the new global coronavirus epidemic, the domestic THT price has risen to more than 4 times the conventional price before the epidemic, and the supply is tight, which brings certain safety risks to the operation and management of gas companies. In addition, the adsorption loss rate of THT in old steel pipes is high. In the case of a substantial increase in prices, it affects the gas company to complete the production and operation goals of reducing costs and increasing efficiency. In contrast, the production cost of sulfur-free odorant is lower, and the adsorption loss rate in natural gas pipeline is lower, which has better economy.

(6) User perception and acceptance

If you want to use a new sulfur-free odorant to replace the traditional THT, you need to consider the end-user 's perception and acceptance of the odor of the new odorant, because the user 's detection and response to the leakage odor is an important part of the safe use of natural gas. It takes a relatively long adaptation time from the user to realize that it is an odor of gas leakage. Therefore, the difference between the odors of the two odorants is one of the difficulties and risk factors of substitution.

4. Application Examples at Home and Abroad

As a large industrial country, Germany pays great attention

to the protection of the natural environment while the rapid development of science and technology. Since 1993, Germany has begun to develop sulfur-free odorants to provide sulfur-free natural gas and reduce operating costs. The world 's first sulfur-free odorant is Gasodor S-Free produced by German Symrise GmbH & Co. KG company. [7] In 1998, it was officially approved by the German Gas and Water Science and Technology Federation (DVGW). Extensive field tests were conducted on the safety, reliability, and tolerance of this new odorant. Since the sulfur-free odorant was put into the market in 2004, Germany 's Saar Long-distance Gas and SWT Company, Dortmund City, Shihe Prefecture and Hamburg City completed the conversion of sulfur-free odorants in 2004,2006,2007 and 2008.The proportion of sulfur-free odorants used in Germany reached 30 %, and has expanded to Austria, Switzerland, Russia, the Czech Republic, the Netherlands and Romania and other countries. At present, the vast majority of natural gas odorization in China is still using sulfur-containing THT, but many gas companies have tried to add sulfur-free odorizer to the urban gas pipeline network. Through the comparative analysis of the test results of tetrahydrothiophene and sulfur-free odorizer, the adaptability of replacing tetrahydrothiophene in urban gas business is evaluated [3].

In 2008, Beijing PetroChina Kunlun Gas Co., Ltd.carried out a test of natural gas sulfur-free odorant Gasodor S-Free on an independent branch pipe network within its gas supply range. The length of the test pipe section was about 13 km, the design pressure was 1.6 MPa, the pipe diameter was DN450 ~ DN150, and the pipeline operating pressure was 0.8 MPa ~ 1.2 MPa.After the successful completion of the conversion, the CMS portable colorimetric tube detector of DRAGER Company in Germany was used to detect the odorant. No crystallization or polymerization was found during the operation of the pipe network. The final test results show that the sulfur-free odorant gasifies and diffuses rapidly, but the early loss is serious. The maximum loss is 70.8 % in the first two weeks after the release, but then the loss is significantly reduced and gradually stabilized. It is speculated that it may be related to the impurities and liquids in the pipeline, and the staff participating in the test have shown consistent praise for the application effect of the sulfur-free odorant in the actual project [2].

In 2013, Huayou Group Xingneng Natural Gas Co., Ltd.of Southwest Oil and Gas Field Co., Ltd.used THT and sulfur-free deodorizing agent to deodorize Honghe gas distribution station and Tianyi skid-mounted cabinet within its gas supply range, and used gas chromatograph to detect and compare the test data. The final results show that the odorization effect of the two odorants will not be significantly affected by factors such as gas supply volume, gas consumption period, and gas supply season. However, the sulfur-free odorant has a faster dispersion in the gas pipeline network, and the distribution is more uniform than THT. The loss rate is lower than THT, and the operating pressure of the pipeline network will have a certain impact on the odorization effect of THT, but it will not have a significant impact on the odorization effect of sulfur-free odorants. In addition, the test project also verified that the sulfur-free odorant has better volatility and cleanliness than THT.If the clothing is contaminated with THT or after the maintenance personnel completes the maintenance work of the gas leakage, the irritating odor of THT is difficult to completely dissipate in a short period of time, and the odor remains for a long time, which will affect the living and working environment of the personnel, while the sulfur-free odorant is more volatile. When the sulfur-free odorant is contaminated on the clothing or exposed to the air, it can be easily cleaned, and its irritating odor will be completely eliminated in a short period of time, which will not cause trouble to people 's life and production. [3].

It can be proved from the above engineering examples that the irritating odor of the sulfur-free odorant can also achieve the warning effect, and the physical and chemical properties are relatively stable. In the conversion process, there is no need to replace the new equipment on a large scale, showing good adaptability to the existing equipment, and no chemical reaction occurs after mixing with THT.In addition, the sulfur-free odorant is obviously superior to THT in terms of diffusivity, volatility, economy, environmental protection and uniformity after mixing with natural gas. Therefore, the sulfur-free odorant has the feasibility of replacing THT in the practical application process.

4. Summary

In recent years, significant progress has been made in the research of sulfur-free odorants in the natural gas industry. Sulfur-free odorants not only have gradually made breakthroughs in odorizing effects, but also have shown advantages in environmental protection, safety and economy. Especially in the natural gas market that requires high quality and low pollution, sulfur-free odorants will become the first choice. However, the basic research work on sulfur-free odorants in China is relatively backward, and there are still some problems and challenges in the future research and development process. Future research can focus on optimizing the formulation and odorization technology of sulfur-free odorants to improve their performance in practical applications. In addition, the standardization and normalization of sulfur-free odorants also need to be strengthened to ensure their effectiveness and reliability in practical applications.

In general, natural gas sulfur-free odorants have shown great potential in replacing traditional sulfide odorants. In the future, the research and application of sulfur-free odorants will continue to develop in the field of natural gas treatment, especially in the pursuit of cleaner and safer energy production and use. With the continuous advancement of technology and changes in market demand, natural gas sulfur-free odorants will gradually become the mainstream choice in the field of natural gas treatment and contribute to the sustainable development of the natural gas industry.

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