Research Progress and Comments on Cracking Agent

Xiaobo Liu, Jiping Liu*, Shukui Li, Junyi Du, Weiwei Yang
School of materials science & engineering, Beijing Institute of Technology, Beijing 100081

* Corresponding author. E-mail: liujp@bit.edu.cn

Abstract. Cracking agent is an important product related to the national energy exploitation and large-scale infrastructure construction. It mainly includes mine explosives, static cracking agent and thermal expansion cracking agent. This article reviews the types, performance characteristics, application conditions, and advantages and disadvantages of the three types of cracked stone products, providing useful reference for the industry development of cracking stone-related applications. This study believes that the thermal expansion cracking agent as a new type of cracking agent with a salient feature of safety, reliability, high efficiency and environmental protection, its performance is better than mining explosives and static rip cracking agent, and this study is an important direction for the future development of cracking agent. In certain fields, it can completely replace mine explosives and static rip crackers and scale it up.

1. Introduction

Cracking agent refers to the generic name for a variety of products that can be used in the fields of rock crushing, stone cutting, demolition of concrete foundations, and demolition of bridges. It is an important product that relates to national energy extraction and large-scale infrastructure construction. According to the development time sequence, the existing ripstone products can be classified into three categories: mine explosives, static rip crackers and thermal expansion cracking agents.

Mine explosives include black powders, slushy explosives, emulsion explosives, and some military explosives. They are important parts of the production process of mines in the past and are widely used in many other fields. However, there are many problems in product toxicity, storage, sensitivity, power, cost, efficiency, safety, and environmental protection, which greatly limit the application of mineral explosives. Many provinces and cities in the country have severely restricted the use of mining explosives. Static cracking agent utilizes the expansion pressure generated by hydration to crack stone. Compared with industrial mine explosives, it has the advantages of silent, controllable, no debris, construction and transportation safety, and is widely used in stone cutting, rock crushing and other fields. However, there are also long periods of cracked rock, low efficiency and labor efficiency of fractured rock, complex process of use, large water requirement, apparent waste of water resources and obvious environmental pollution, and other fatal weaknesses. The thermal expansion cracking agent is a new type of cracking stone product that is completely different from the existing explosives and static cracking agent. It is a combination formula developed by the Beijing Institute of Technology to provide technical support and is jointly developed with Guizhou Runjin Carbon Element Materials Co., Ltd. The product not only played the advantages of local natural resources in Guizhou Province, but also met the requirements of high efficiency, safety and environmental protection for the mining industry at this stage [1-3].
This article gives a comprehensive review of the product characteristics, application and research progress of the three types of cracked stone products, and provides useful reference for the development of cracked stone products and related industries.

2. Mine Explosive
Mining explosives are the support of modern mining, tunnels, and water conservancy industries. They are explosives prepared by mixing oxidants and combustion agents. Black powder is the earliest used mine explosive and was used in the mining industry in the 17th century. In the 19th century, with the invention of Nobel Nitroglycerin explosives and the appearance of ammonium nitrate explosives, the types of mine explosives were further enriched. After entering the 20th century, ammonium oil explosives, pulverized explosives, and emulsion explosives have emerged one after another and have gradually become the main category of mine explosives. In addition, some military explosives were also temporarily used as mine explosives in special or large-scale projects.

There are many classification standards for mining explosives. From an industry point of view, safe use is the first classification criterion. The classification should be based on this. According to the different characteristics of explosives and the environmental conditions of use, especially considering the environment with gas or dust explosion hazards, mining explosives are first divided into general mining explosives and coal mine safety explosives. The latter incorporates a flame arrester and is specifically designed for use in mines where gas or coal dust explosion hazards exist. When blasting operations are carried out, the corresponding explosive species must be selected in strict accordance with the mine gas emission level and other mining conditions. According to the different chemical compositions and properties of explosives, commonly used mineral explosives can be divided into three categories: ammonium oil explosives, emulsion explosives and liquid explosives. Each category is divided into several types.

2.1. Ammonium oil explosives
The main components of ammonium oil explosives are ammonium nitrate and fuel oil. According to the scope of use, ammonium nitrate explosives can be divided into rock ammonium oil explosives, coal mine ammonium oil explosives and open-air ammonium oil explosives. According to the composition, ammonium nitrate explosives can be divided into ordinary ammonium oil explosives and special ammonium oil explosives. According to the ammonium nitrate particle size can be divided into powdered ammonium oil explosives, granular ammonium oil explosives and porous granular ammonium oil explosives. Among them, porous granular ammonium nitrate is a high-porosity particle filled with holes inside. The internal pores not only ensure the sucking of fuel oil, but also increase the detonation sensitivity and detonation sensitivity of the system, thus forming a new type of ammonium nitrate explosive with unique physical properties and explosive performance. With the advantages of safe transportation, storage, strong oil absorption, no caking, etc., it is suitable for on-site mixing and mechanization. In contrast, powdered ammonium oil explosives are not as good as granular ammonium oil explosives in terms of production process, cost, labor force, and so on.

At present, ammonium oil explosives are widely used in China's metallurgical mines, but the shortage of porous granular ammonium nitrate in the domestic market has severely restricted the expansion of the scope of application of granular ammonium oil explosives and further improvement of the use of technology.

2.2. Emulsion explosives
Emulsified explosives refer to the use of emulsion emulsifiers to emulsify emulsions to form water-in-oil emulsions and sensitize explosive mixtures. Specifically, the emulsion explosive is a special water-in-oil emulsion system. The fine droplets of an aqueous solution of an oxidizing agent such as ammonium nitrate are used as the dispersed phase. The continuous phase is a water-insoluble or oil-containing combustible component containing dispersed bubbles or hollow glass microspheres or other porous materials. Among them, the aqueous oxidizer solution is in intimate contact with fine
droplets and combustible components. Through the water-in-oil emulsifier membrane formed at the interface between the internal and external phases to obtain good water resistance, to prevent the delamination of the oil and water components, demulsification, making the explosive detonation of the explosive explosive and easy to transfer [4]. Emulsion explosives concentrate the advantages of ammonium oil explosives, slurry explosives, and water-based explosives. It has the advantages of good explosion performance, convenient processing, safe use, no pollution, strong water resistance, abundant raw materials, and explosive products containing less toxic gases, etc. It has become the most widely used industrial explosive in its current scope and conditions.

Emulsion explosives still have many problems. Among them, the most basic issue is stability. The emulsion system itself is an unstable thermodynamic system that cannot maintain its long-term physical state and its explosive performance does not change significantly. Stratification, deformation, and loss of certain or all detonation abilities occur during storage at room temperature, resulting in poor emulsion stability, short shelf life, and inconvenience in production, storage, and use. In addition, emulsion explosives generally have practical problems such as low energy density, high cost, high viscosity, and difficulty in manual loading. In cold regions, especially in regions where the temperature is below -20 °C, the detonation performance of the emulsion explosive will decline or even deny [5], which greatly limits its application. In recent years, on-site mixed emulsion explosive technology has realized the integration of production, distribution, and blasting operations of emulsion explosives, and has become a new technology popularized by civil explosives [6].

3. Static cracking agent
Static cracking agent is a powdery substance composed of inorganic compounds and special organic substances. Mix it with water and fill it into a hole in a rock or concrete object. After a period of chemical reaction, the swelling pressure produced by hydration can cause the rock to disintegrate silently.

There are many formulations for static cracking agents, such as the preparation of mineral powders in a certain proportion with limestone, silica and gypsum, or the addition of hydraulic materials and mixtures in quicklime. The commonly used cracking agent ingredients are expanded free quicklime and calcium sulfoaluminate. Among them, the free lime has great hydration swelling power, but its hydration heat accumulation can easily cause the steam pressure to rise, causing the filled cracking agent to spray. After adjustment and optimization, these cracking agent products include: static cracking agent mainly composed of free lime and tricalcium silicate, static cracking agent consisting of hard lime, cement, water reducer, static cracking agent composed of calcium oxide and calcium carbonate, heat-treated and hydraulically solidified, a coagulant, and a water-reducing agent, and static limestone composed of quicklime and chloride [7].

Before the use of static cracking agent, the construction design is generally carried out. According to the application objects and conditions, calculate the amount of static cracking agent required for cracking stone, and calculate parameters such as pore size, hole spacing, row spacing, hole depth, and distribution. After drilling according to the calculation results, the cracking agent is filled in the rock or concrete hole, waiting for cracking. Therefore, the static lithoclastic rock-breaking process has the characteristics of low-pressure expansion, slow-loading, no vibration, no noise, no flying rocks, no toxic gas, and the rock-breaking agent itself is inflammable and non-explosive, and production, storage, transportation and use are very safe. It is suitable for mining, cutting, crushing, loosening of concrete, dismantling of concrete foundations, crushing construction of roads, bridges and tunnels. It is especially suitable for situations where partial crushing or dismantling is required but it cannot affect or destroy the whole.

However, in actual applications, static cracking agents also have fatal disadvantages. The cracking time of this type of products is too long, and the efficiency of cracked stone is too low. Compared with industrial explosives, even static cracking has many advantages, which greatly affects the enthusiasm of most users. In addition, the use of static rip crackers requires a large amount of water, waste of
water resources and environmental pollution, and does not meet the development needs of modern green industry.

4. Thermal expansion cracking agent

As a new type of cracked stone product, thermal expansion cracking agent adopts the concept of organic combination and comprehensive utilization of plant waste and mineral waste. For the first time, commonly used raw materials such as straw and coal gangue are used for thermal expansion cracking agent, and the best cracking effect is achieved through a certain process. Specifically, coal-based carbon black, coal gangue, straw, calcium peroxide, potassium perchlorate, and starch are used as raw materials, and the mixture is then pulverized, kneaded, granulated, dried, and the like. Its products are in the form of granules, which can be filled in the boreholes to meet the requirements of the filling density of cracked stones. The operation is simple, safe and reliable. The product has good dispersion and antistatic properties and is safe and stable in storage. The raw materials needed for product preparation are widely sourced and low in cost.

Thermal expansion cracking agent is significantly different from existing static cracking agents and explosives in terms of product properties, formulation composition, cracking principle, and usage methods. The thermal expansion cracking agent uses the pressure generated by the instantaneous gas expansion to crack the rock, releasing more heat through the chemical reaction. The high temperature generated by the heat release can heat and destroy the surrounding medium, and some of the generated gas can work on the surrounding medium due to the high temperature thermal expansion. Due to the small amount of generated gas and the loose bulk of the thermal expansion agent, the gaps between the thermal expansion agent and the self-compression effect between the particles achieve the expansion buffer of the thermal expansion cracking agent. The effective conversion of remote power to short-range power is achieved, and the effective accumulation of the thermal expansion rock-cracking agent's expansion energy can be achieved during the effective work time. At the same time, it avoids the loss of work caused by the rapid leakage of hot expanding gas. The thermal expansion gas can only form a very weak expansion pressure and the pressure decays rapidly, and can only effectively perform work within a short distance of several meters. The scope of doing work is small and the efficiency of doing work is high. Therefore, the thermal expansion cracking agent has the advantages of being micro-sound, controllable, fast, safe and reliable during use, and the use process is clean and free of water and has no pollution to the environment, and can be exploited in the mining, rock crushing, trench caisson, etc. Demolition of concrete foundations and other fields are applied.

5. Conclusions

The development of a safe, reliable, environmentally friendly, convenient, and efficient ribble agent is a key and necessary step in the current development of the mining industry. It is also urgently needed for large-scale infrastructure construction and demolition projects. Mine explosives as traditional ripstone products have similar advantages and disadvantages. Mining and pollution coexist, and high-efficiency and hidden dangers coexist, making mining explosives urgently need an industry innovation. Static cracking agent as a new type of cracked stone products in recent years, its significance of safe construction is far greater than the practical significance. In practical applications, static cracking agent is more inefficient, and there are also problems such as pollution, water consumption and other problems than mine explosives. It will become the core issue that restricts the development of static cracking agents. As a new type of cracking agent, the thermal expansion cracking agent is superior to mine explosives and static cracking agents. It possesses salient features such as safety, reliability, high efficiency and environmental protection. It is an important direction for the future development of cracking agents and can completely replace ore in certain fields. Use explosives and static cracking agents for promotion. However, it is worth noting that, as a new type of product, the shortcomings of thermal expansion cracking agents need to continue to be tested in the industry. In this process, ensuring the timely self-renewal of thermal expansion cracking agent products and constantly
improving the existing defects is the key to the promotion and application of thermal expansion cracking agent.

References
[1] Liu J P, Liu X B, Han Z W, et al. A method of large-area split rock with equal proportion structure of thermal expansion cracking agent. *Beijing* CN105019901A 2015-11-04.
[2] Liu J P, Han Z W, Liu X B., Preparation method of thermal expansion cracking agent. *Beijing* CN104961386A 2015-10-07.
[3] Liu J P, Han Z W, Liu X B, et al. A thermal expansion cracking agent. *Beijing* CN104961387A 2015-10-07.
[4] Li B. Study on the stability of the Emulsion Explosive and the method of Characterizations. *Anhui University of Science and Technology* Huainan China 2008.
[5] Li Z, Li Q, Du Y Y, et al. 2017 *Explosive Materials* 46 22-29.
[6] Zhou W G, Sun L K 2017 *Guangdong Chemical Industry* 44 60, 90.
[7] Zhou Z H 2015 *Stone* 1 24-27.