Department of Chemical Technology and Research of BPCI NAS Ukraine. Intentions and Accomplishments.

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Department of Chemical Technology and Research – DCTR – was created in 1977. Academician Gutyrya V.S., Prof. Sklyar V.T. and Prof. Shkaraputa L.M. defined the core area of research as development of scientific basis of industrial production bioorganic, organic and petrochemical products. They also formulated department's mission statement and philosophy. The core factor in defining these areas was recognition of the fundamental difficulties in transferring laboratory level syntheses and recipes into high volume industrial production. Only by means of creating and employing complex mathematical models to describe the chemical reaction patterns and dependencies, one can develop approaches of efficient large-scale production, creation and optimization of appropriate equipment toolsets. In light of the chosen R&D direction, the efforts of the Department's staff are focused on analyzing the mechanisms, kinetics, thermodynamics, thermo-physics, hydrodynamics of chemical interactions, creating and enhancing chemical process models, developing and optimizing the production equipment, procedures and technical know-how.

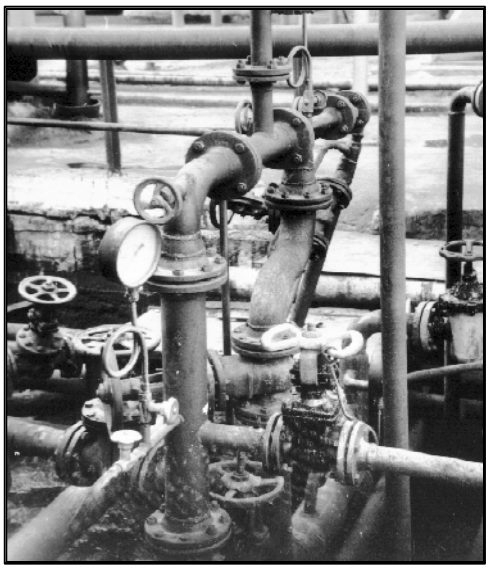
DCTR researchers (Shkaraputa L.M., Kononov O.V., Tyshchenko L.O.) were first to discover that electrophilic addition of chlorine to olefins in water may proceed according to both associative as well as the dissociative mechanisms. Thus, the criterion for differentiating areas of bi- and tri-molecular interaction was uncovered. Based on fundamental chemical acts, for the first time the correlations describing the speed of formation of the products were determined, and conditions enabling determination of the current concentration of olefines vs. conductivity of the reaction mixture were uncovered, thus considerably simplifying determination of kinetic constants. The mathematical expressions that adequately describe the process were established, the algorithm of optimization and calculation of the non-stationary modes were developed, that was realized in the original methods of generating 3-chlor-4-oxy- and 3,4-dichlorotholane-1,1-dioxides (Shkaraputa L.M., Kononov O.V., Sklyar V.T.).

Process sulfatization was also studied by similar approach. The mathematical description of the twin-screw reactor-mixer was formulated that takes into account the regular patterns of transporting, warm-up, crystallization and actual chemical transformation of reagents mixture under continuous evacuation of one of the ingredients. These researches enabled development and successful demonstration of the production process to generate highly-efficient substances for treatment of cotton fabrics "ЛУР" and "ДИМОС" in high volume (Shkaraputa L.M., Sklyar V.T., Bezmenova T.E., Usenko Yu.N., Sidorova O.S.).

DCTR experts proposed effective emulsion stabilizers "ЭС-2", "ЭС-4", "БЭС-1", developed technologies for directed emulsion and acid treatments of the by-face areas, technologies of mining hole muffling by reverse emulsions on the basis of "ЭС-2" emulgators (Sklyar V.T., Kendis M.Sh., Gluschenko V.M.). The thermo-physical and thermo-chemical properties of reagents, thermodynamic and kinetic parameters of interaction between deep blue tailings of SFA and dextramine were studied and the adequate mathematical models of processes in different types of reactors were designed. Based on optimization technological regulations ***were developed to produce 5000 t of "ЭС-2" and "ЭС-4" on Drohobytch oil refinery*** (Shkaraputa L.M., Sklyar V.T., Danilenko V.V., Tabakov A.V.). Production revenues exceeded 30,000,000 soviet roubles.

The department has conducted (Shkaraputa L.M., Bespalyj A.S., Danilenko V.V., Tabakov A.V.) large scale selection of the alternative raw material and development of compounding and technological processes to synthesize composition binders from inefficiently utilized substances and by-products of oil refining (oil slurry, sour tar, asphalt-extract mixtures (AES), tar, rubber wastes, etc) for road construction and coke technology. The ways of affecting quality factors were found. Effective alloying admixtures and accessible catalysts which enable generating binders without involving traditional air oxidation were offered. The new binder recipes were recognized as original inventions. It was shown that the use of cavitation influence not only radically improves component mixing, but due to its high-energy impact enables the factor of 4–12 acceleration of the chemical processes of generating binders via compounding and oxidation. The dependences between geometry of the supercavitational mixer, modes of circumfluence and terms of oxidation were investigated, the mathematical model of the supercavitational mixer and calculation methodology of its construction were created (Shkaraputa L.M., Tyshchenko L.O., Shevchenko L.A.). ***The technology for generating high-quality compositional binders "БШВ", "КВАГУ", "КВАГУ-Б" were developed and implemented at Krementchug oil refinery*** (Shkaraputa L.M., Danilenko V.V., Sklar V.T., Bespaly A.S., Tabakov A.V.) to produce 200,000 tons/year binders for road construction and briquetting of coke. The use of tar, sour tar and oil slurry, promoted improvement of the ecological aspects of production.

DCTR staff studied possibilities to synthesize binders for road building based on oil products with high paraffin content and wastes which had accumulated at Drohobych oil refinery. The department developed recipes for producing high-quality road building binder compounds "КВ", and liquid emulsion composition binders "КВЖ", that were used for macadam blackening and preparation of the road mixture to generate the coating. As a result, ***the industrial production of binders for road construction was established for the first time at Drohobych oil refinery with production volumes of 20 thousand tons per year based on original technological process***.



Hundreds of thousands of tons of binders "БШВ", "КВАГУ", "КВАГУ-Б", "КВ" and "КВЖ" have been produced. Implementation of these technological processes for production of compositional binders allowed significant reduction of energy costs while utilizing sour tar, oil slurry, wastes, and practically eliminating harmful emissions into the atmosphere.

The practical experience to work with by-products and wastes of oil refining enabled to offer (Shkaraputa L.M.) facilities to curb dust formation in the site of Chernobyl Nuclear Power Plant after disaster in May, 1986. For dust suppression on the roads it was recommended to apply oil slurries and oil refining wastes accumulated at oil-processing factories. The effectiveness of this oil slurry based methodology was proven in Chernobyl. The mobile layer of soil particles were saturated with oil products and formed films, which prevented dust migration, even when been destroyed under the tires of heavy trucks. ***The specifications on oil slurry and technological recommendations for dust suppression were developed and over 10 thousand tons of slurry were used in May–June 1986 under the direction of DCTR employees*** (Shkaraputa L.M., Manojlo O.I.)

The original synthetic decontamination detergent composition was designed (Krentkovska O.J., Shkaraputa L.M., Kukhar V.P.) ***and applied at Chernobyl Nuclear Power Plant*** for decontamination and laundering of clothing and sheets in cold water (from +5 °C) based on the special assignment from the Ukraine Ministry for Chernobyl. The production technology was developed, the experimental lots of the new synthetic detergent and decontamination composition was produced and proved its effectiveness at JV "Complex".

DCTR has offered the alternative sources of raw materials for synthesizing technological oils used in steel wire drawing. The original compound was synthesized for this purpose, which exceeded by the factor of 1,5–2 the operational parameters of all known alternatives, and the process technology was developed (Danilenko V.V., Shkaraputa L.M., Kendis M.Sh.).

Per the request from the Ministry of Construction, its were developed synthetic hydrophobic coatings of cardboard air-ducts for use in heating and air circulation systems (Bespalyj A.S., Shkaraputa L.M., Danilenko V.V.). Experimental lot of such air-ducts passed all testing successfully.

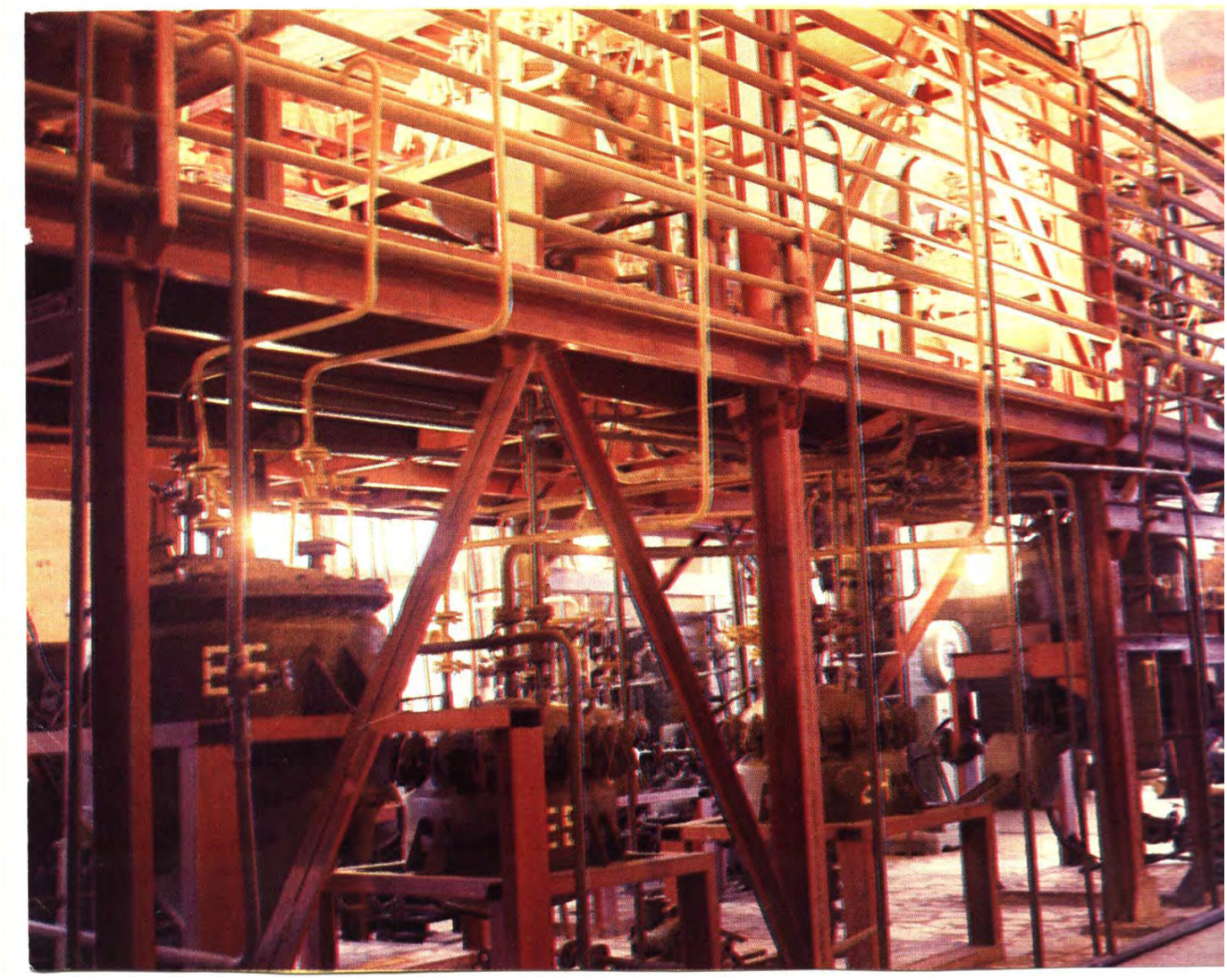
Research and development of emulsifiers and inhibitors was extended into the area of corrosion inhibitors for oil production equipment, new recipes and technologies were created. New recipes for synthetic inhibitors for these targets without hydrogen sulfide, the "Дорад-11", and with hydrogen sulfide, the "Дорад-1ВЦ" were designed (Shkaraputa L.M., Sklyar V.T., Danilenko V.V., Tabakov A.V.). Their operating characteristics drastically exceed the characteristics of the known inhibitors, while their cost is the factor of 2 lower. The "Дорад-1ВЦ" inhibitor was tested at "Buzuluknafta", with its high efficiency proven experimentally, while tests at Poltava NGBY proved effectiveness of "Дорад-11" product.

In 1992 the development of technology to produce the equivalent of azidothimidine ("Теозидин"), the HIV treatment drug, was started. Using developed stage-by-stage process control, the optimization of "Теозидин" synthesis by route D-glucose – 2-desoxy-D-ribose – thimidine – "Теозидин" was successfully realized (Shkaraputa L.M., Kononov O.V., Polyakov O.D., Danilenko V.V., Yazlovitsky A.V., Lushnik I.S.) and high quality thimidine was prepared. The preclinical study of "Теозидин" was conducted, its identification tests were developed, it's specific action and margin toxicity were studied. The main conclusion of the virologists was that "the inhibiting action of the domestic drug is equivalent to that of Retrovir", and that "we may ascertain the similarity of symptomatic outcomes of the corresponding reactions to toxic influence of the AZT ("Теозидин") substance and Retrovir drug". The State Scientific and Research Institute "Khimfarmproekt" conducted analysis of "Теозидин" R&D and volume production location. Principal technological schemes were developed to produce the substance on the Cherkassy Chemical Reagents Plant. It was calculated that the cost of 1 kg of "Теозидин" would be significantly lower in comparison with Retrovir, produced by "Velkom" and "Тимазид", produced by the Russian association "AZT. Thus, the production of domestic "Теозидин" should save Ukraine from $2,000 to $9,000 for every kilo of the drug. Also ***efficient synthesis of AIDS treatment drug D4T was also developed***, the process control and the technological recipes were developed. The D4T samples were prepared for preclinical tests (Shkaraputa L.M., Kononov O.V., Polyakov O.D.).

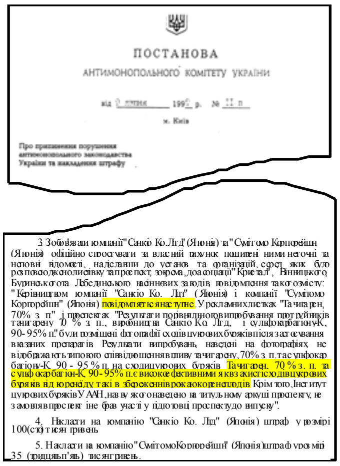
Unfortunately the top managers of Ukraine Committee on AIDS showed lack of interest in organization of domestic HIV inhibitors production and further financing of the development and scale production of AZT and D4T was stopped.

At the same time the importance of such research was manifested in the State Award by the Russian Federation given to the ex-employee of DCTR O.V. Kononov for development of the Russian equivalent of AZT.

In the early 1980-s potassium N-(1,1-dioxothiolan-3-yl) dithiocarbamate was synthesized. The compound was called "Сульфокарбатион-К" (СКК). Out of many thousands of synthesized compounds only very few passed biological, toxicological and ecological tests are economically viable and become commercial products. Certification of agrochemicals is a very long and complex process, which typically requires around 1000–1500 man-years and 50–100 Millions of US dollars. While developing CKK technology the key chemical reactions were studied precisely. Detailed understanding of amination of 3-thiolen-1,1-dioxide enabled .to find original catalysts of the process which allowed to accelerate the reaction in 6–8 fold and to boost both efficiency and selectivity of the process. The kinetic and thermodynamic parameters, thermo-physical characteristics of the reaction mass were investigated and the adequate mathematical models of the process were created. The optimum process parameters were determined: the process duration was shrunk from 28–48 hours to 2–4 hours, a pressure was reduced from 25–30 to 3–5 atm, and a problem of ammonia recycling was resolved. The experimental verification showed that the product yield increased from 76–80 % to 93–98 %, and the selectivity – from 76–86 % to 95–99 % (Shkaraputa L.M., Kononov O.V., Sidorenko V.M., Sklyar V.T., Danilenko V.V.). Previous attempts to synthesize even small amounts of "Сульфокарбатион-К" showed that the previously known dithiocarbamination methods were unsuitable for industrial production due to low yield, considerable toxicity of target product and big amount of waste generated. DCTR researchers uncovered conditions for high-selectivity generation of dithiocarbamates and proved the effectiveness of programmable delivery of the initial ingredients into the reaction area. As a result of conducted research, the mechanism of reaction between amines and carbon disulfide was revised (Shkaraputa L.M., Kononov O.V., Polyakov O.D.). The regular patterns of dithiocarbamination in the variable mass reactor were described quantitatively. The optimum distribution of reagents introduction was determined. ***The original methods of CKK production were developed and the set of the experimental installations was designed and constructed allowing production of up to 20 tons of CKK per year*** (Shkaraputa L.M., Sklyar V.T., Zhukovsky V., Danilenko V.V., Abrosimov V.F., Gusak V.G.). ***CKK is now utilized across nearly 800 thousands of hectares of farmlands.***



"Сульфокарбатион-К" is registered as the protectant for seeds of sugar beets, wheat, corn, barley, rape, buckwheat, millet and potato sprouts (Shkaraputa L.M., Sasinovich L.M., Danilenko V.V., Kotenko S.I., Tyshchenko L.O., Shevchenko L.A.). It allows 2 to 3



ПОСТАНОВА
АНТИМОНОПОЛЬНОГО КОМІТЕТУ УКРАЇНИ

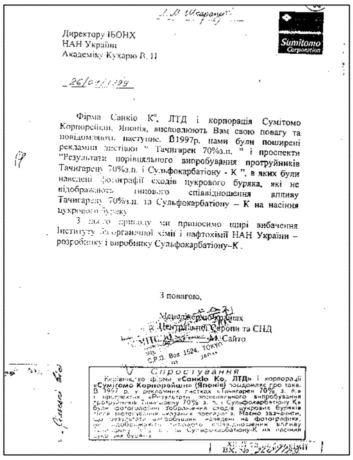
м. Київ

Про припинення порушення антимонопольного законодавства України та накладення штрафу

3. Зобов'язати компанії "Санкіо Ко. Лтд" (Японія) та "Сумітомо Корпорейшн" (Японія) офіційно спростувати за власний рахунок поширені ними неточні та неповні відомості, надіславши до установ та організацій, серед яких було розповсюджено листівку та проспект, зокрема, до асоціації "Кристал", Вінницького, Буринського та Лебединського насіннєвих заводів, повідомлення такого змісту: "Керівництвом компанії "Санкіо Ко. Лтд" (Японія) і компанії "Сумітомо Корпорейшн" (Японія) повідомляється наступне. У рекламних листках "Тачигарен, 70% з. п." і проспектах "Результати порівняльного випробування протруйників тачигарену 70 % з. п., виробництва Санкіо Ко. Лтд, і сульфокарбатіону-К, 90-95% п." були розміщені фотографії сходів цукрових буряків після застосування вказаних препаратів. Результати випробувань, наведені на фотографіях, не відображають типового співвідношення впливу тачигарену, 70% з. п. та сульфокарбатіону-К, 90 - 95 % п. на сходи цукрових буряків. Тачигарен, 70 % з. п. та сульфокарбатіон-К, 90-95% п. є високоефективними як в захисті сходів цукрових буряків від коренеїду, так і в збереженні врожаю коренеплодів. Крім того, Інститут цукрових буряків УААН, назву якого наведено на титульному аркуші проспекту, не замовляв проспект і не брав участі у підготовці проспекту до випуску".

4. Накласти на компанію "Санкіо Ко. Лтд" (Японія) штраф у розмірі 100 (сто) тисяч гривень.

5. Накласти на компанію "Сумітомо Корпорейшн" (Японія) штраф у розмірі 35 (тридцять п'ять) тисяч гривень.



Директору ІБОНХ
НАН України
Академіку Кухарю В. П.

26/01/1999

Фірма Санкіо К°, ЛТД і корпорація Сумітомо Корпорейшн, Японія, висловлюють Вам свою повагу та повідомляють наступне. В 1997р. нами були поширені рекламні листівки " Тачигарен 70%з.п. " і проспекти "Результати порівняльного випробування протруйників Тачигарену 70%з.п. і Сульфокарбатіону - К ", в яких були наведені фотографії сходів цукрового буряка, які не відображають типового співвідношення впливу Тачигарену 70%з.п. та Сульфокарбатіону – К на насіння цукрового буряку.

З цього приводу ми приносимо щирі вибачення Інституту біоорганічної хімії і нафтохімії НАН України – розробнику і виробнику Сульфокарбатіону-К.

З повагою,

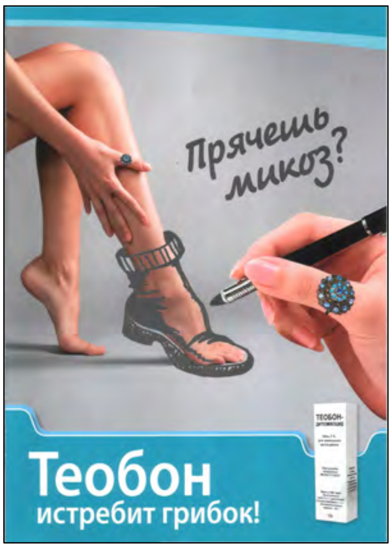
Менеджер по країнах
Центральної Європи та СНД
М. Сайто

Спростування

Керівництво фірми «Санкіо Ко, ЛТД» і корпорації «Сумітомо Корпорейшн» (Японія) повідомляє про таке. В 1997 р. у рекламних листках «Тачигарен 70% з. п.» і проспектах «Результати порівняльного випробування протруйників Тачигарену 70% з. п. і Сульфокарбатіону К» були фотографічні зображення сходів цукрових буряків після застосування вказаних препаратів. Маємо зазначити, що результати випробувань, наведені на фотографіях, не відображають типового співвідношення впливу Тачигарену 70% з. п. та Сульфокарбатіону-К на насіння цукрових буряків.

fold reduction in costs associated with preparing wheat seeds, significantly increasing production yields. CKK application methodologies were recognized as original inventions. The Ministry of Agrarian Policy has defined the need for products of this group in the amount of ≈3000 tons per year. Introduction of CKK resulted in investments of over $200,000 in Ukrainian economy. World-famous Japanese companies ***"Sankio Ko Ltd" and "Sumitomo Corporation" have officially recognized that "Сульфокарбатион-К" was on par with one of their flagship products – protectant Tachigaren***. There wasn't a single agrochemical in this class developed throughout the entire history of USSR and independent Ukraine. Later on, based on the success of CKK, a whole series of chemical methodologies was developed for plant protection via the surface contact mechanism (Shkaraputa L.M., Danilenko V.V., Alimova O.V., Kotenko S.I.).

By expanding the methodology of generating N(1,2-dioxothiolan-3-il) potassium dithiocarbamate jointly with the National Medical Academy the original highly effective antimycotic drug "Теобон-дитиомикоцид" was conceived and its technological processes developed and optimized (Shkaraputa L.M., Kononov O.V., Sasinovich L.M., Danilenko V.V., Tyshchenko L.O., Shevchenko L.A., Kolyadenko V.G., Stepanenko V.I.). Research of its toxicity and specific activity was showed that it is much safer than the majority of antimycotics and antiseptics. It suppresses the malignant fungi *Candida albicans*, *Candida tropicalis*, *Trichophyton rubrum*, *Microsporum canis*, etc, and a number of bacteria of intestinal and coccal groups.



The clinical trials of this drug showed that it is safer and more effective than the known klotrimazol and mikozolon drugs, and that it enables to shorten the treatment term by 25 %. The Ministry of Health of Ukraine has registered the substance "Теобон-дитиомикоцид" and the two medical forms cre-

ated on its basis (one – ointment and one – powder for solution preparation). ***309 anti-fungal drugs were registered in Ukraine's history with only two of them developed domestically in Ukraine and one of these two drugs was "Теобон-дитиомикоцид"***. The production of ointment "Теобон-дитиомикоцид" was established with nearly 65,000 packs sold to date.

Application of extruded polyolefin coatings is one of the most effective means of passive anticorrosive protection. Their unique advantage is high physical-mechanical, dielectric and anticorrosive properties. However, such isolating coatings are typically applied when pipes are heated to 150–220 °C (Shkaraputa L.M., Mitrokhina L.L., Morozova I.P., Alimova O.V., Abrosimov V.F.). Department researchers ***have designed original materials which enable application of the extruded polyethylene coatings at as low temperatures as 15–20 °C***. The series of tests conducted by NBP "Ukrtruboizol" plant has experimentally proven that the coatings developed at DCTR had much better adhesion to steel and exceeded the DSTU 4219, GOST R 51164 and DIN 30670 standard specifications, while their radius of sheet detachment during cathode polarization was only 2–3 mm, with the specification of up to 11 mm. At the same time their production, installation and maintenance costs can be significantly reduced by eliminating the need for expensive pipe heating, cooling and chemical deposition on equipment. ***This newly-developed "cold" surface coating technology is on par with the world's leading edge methodologies.***

Departments' list of publications includes 3 books and 300 journal articles, while 70 patents were granted. Two of the researchers were granted Doctor of Sciences Titles, while eight – defended Candidate of Sciences Dissertations. For the past 12 years Department members supported review and publication of the "Catalysis and Petro-chemistry" journal (Tyshchenko L.O., Shevchenko L.A., Shkaraputa L.M.).

Apart from the aforementioned experts, the list of researchers who provided significant contributions to the department's achievements includes Cherednichenko V.I., Gordienko A.G., Tereshchenko V.A., Matyash L.P., Kuznetsov V.O., Gisar K.V., Sklyar V.T., Rudenko L.I., Zinov'eva L.V., Gusak V.G., Gusak G.P., Voronova O.S., Novitskaya L.D., Lebedeva O.E., Zaika T.D., Mironova Z.M., Schur V.P., Evseeva L.S., Litvinenko V.M., Leychkis I.M., Ischuk S.Yu., Hrutba V.O., Popsuyko O.M., Han V.-E., Vorontsova L.S., Nazarova N.I., Shaporenko T.V., Belova N.A., Tumanyan O.I., Makovej N.M., Manoilo O.M., Kalashnikov M.B.

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Відділ хіміко-технологічних досліджень. Наміри і досягнення.

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Відділ хіміко-технологічних досліджень (нафтохімічної технології) створено у 1977 році. Основний напрямок досліджень, мета, ідеологія всієї роботи – розробка наукових засад промислового виробництва продуктів біоорганічного, органічного та нафтохімічного синтезу, сформульовано академіком В.С. Гутирею, д.т.н., проф. В.Т. Скляром і д.т.н., проф. Л.М. Шкарапутою. При визначені наукового напрямку визначальним було розуміння неможливості і недоцільності простого переносу умов лабораторного синтезу у промисловість. Тільки створення та дослідження математичних моделей, що достовірно описують закономірності хімічного перетворення, може виявити шляхи раціонального виробництва, вирішити питання масштабування, апаратурного оформлення і оптимізації. У межах вибраного наукового напрямку зусилля співробітників відділу зосереджені на проведенні аналізу механізмів хімічної взаємодії, дослідженні кінетичних, термодинамічних, теплофізичних та гідродинамічних закономірностей, створенні та дослідженні математичних моделей процесів, оптимізації, вирішенні питань апаратурного оформлення, розробці технологічних регламентів, технічних умов, створенні та освоєнні установок та вирбництв.

Отдел химико-технологических исследований Намерения и достижения.

Л.Н. Шкарапута

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Отдел химико-технологических исследований (нефтехимической технологии) создан в 1977 году. Основное направление исследований, цель, идеология всей работы – разработка научных основ промышленного производства продуктов биоорганического, органического и нефтехимического синтеза, сформулированы академиком В.С. Гутырей, д.т.н., проф. В.Т. Скляром и д.т.н., проф. Л.Н. Шкарапутой. При определении научного направления определяющим было понимание невозможности и нецелесообразности простого переноса условий лабораторного синтеза в промышленность. Только создание и исследование математических моделей, достоверно описывающих закономерности химического превращения, может выявить пути рационального производства, решить вопрос масштабирования аппаратурного оформления и оптимизации. В рамках выбранного научного направления усилия сотрудников отдела сосредоточены на проведении анализа механизмов химического взаимодействия, исследовании кинетических, термодинамических, теплофизических и гидродинамических закономерностей, создании и исследовании математических моделей процессов, оптимизации, решении вопросов аппаратурного оформления, разработке технологических регламентов, технических условий, создании и освоении установок и производств.