significant alteration of the ecological situation in our country. The main reason for this unsatisfactory situation is inadequate interest in industrial undertakings in measures for the protection of nature. In my view, there is only one solution to the problem which has arisen: the universal introduction of fines for exceeding the level of harmful emissions above the permitted limit. A reasonable approach is necessary both to the selection of the initial magnitude of the fines and to the dynamics of their increase as a function of time. Both these parameters must be chosen so that industrial undertakings are encouraged to introduce more rapidly nature-protecting technologies without going at the same time beyond the limits of realistic possibilities.

From statements made by the leaders of the State commission on Nature in the USSR, we known that the inevitable introduction of fines is expected at the beginning of the next five year plan and that proposals for the appropriate resolutions are being prepared. They suggest that it would be right to publish these proposals as quickly as possible, so that they can be discussed in good time and also to make sure that workers of the industrial undertakings and in transport should be convinced of the reality of the coming fines.

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Ecological aspects of the production and consumption of hydrogen

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The world annual production of hydrogen is about 50–60 million tonnes, including that of the USSR which is about 6 million tonnes. Natural gas is the major raw material for the production of commercial hydrogen; the amount of hydrogen obtained by electrochemical methods is not greater than 1–2% of the total.

Virtually all hydrogen produced is consumed within the chemical industry, in particular for the production of ammonia and nitrogeneous fertilisers. In the decades ahead, it is expected that not only will hydrogen production increase (to 80–100 million tonnes annually), but also the structure of its consumption will change. It is also predicted that the use of hydrogen in the national economy will increase in an effort to create ecologically clean power generation and fuel technology for transportation facilities, to increase substantially the efficiency of oil refining and to use coal as the raw material for the production of synthetic fuel. Even nowadays, a small admixture of hydrogen to motor fuels would assist in overcoming a number of regional environmental problems, primarily those of increasing pollution of the atmosphere by carbon monoxide and carcinogenic products from the combustion of organic fuels, prevalent in large cities and opencast mines, which produce ore, coal, and other minerals.

Hydrogen is assuming special importance in low-volume high-technology branches of industry, such as electronic and pharmaceutical, in the production of high-purity metals and alloys, composite materials, chemically highly active substances, catalysts, and the like.

In the mid-1970's, the possibilities of the widespread use of hydrogen in the national economy as an alternative fuel or energy carrier were considered in the context of the so-called "energy crisis". At that time, however, various approaches to energy problems, based on the concept of hydrogen energy system, despite its apparent logic and attraction, were not supported by the necessary volume of research and development work. What is more, in engineering and economical respects the above approaches lost the competition with alternative ideas for the development of power engineering complexes based on high-performance energy-saving technologies.

At present, owing to the worldwide deterioration of the ecological situation, hydrogen is again actively considered as an alternative fuel and hopes are being placed on it. This feeling was expressed by the US participant at the 7th International Conference on Hydrogen Energy Systems, held in Moscow in October 1988. The use of hydrogen "gives humanity a unique change to survive in the world, rescued from ecological and social disasters", he said in his concluding remarks.

It is worth quoting some figures which illustrate how acute is the ecological problem associated with the combustion of organic fuel. In recent years, the industrial emission of carbon dioxide has been in excess of 5 billion tonnes annually, while that of carbon monoxide was in the range of 100–200 million tonnes annually. The emissions increased by a factor of 3.5 compared with their level in the 1950's and the tendency to increase is continuing: by the year 2000, the amount of carbon dioxide entering the atmosphere will rise to 6.0–6.5 billion tonnes annually, whilst that of carbon monoxide will rise to 250–300 million tonnes annually. Motor transport is responsible for up to 20% of CO_2 and (depending on the region) for 60–90% of CO emissions. For example, during the period 1985–1988, 800 000 trucks and diesel buses, which formed part of the Moscow fleet, ejected into the atmosphere about 200–250 thousand tonnes of carbon monoxide annually, excluding carcinogenic smoke resulting from incomplete combustion and pyrolysis of organic fuels.

However, in order to pave the way for hydrogen energy systems, including ecologically clear transport, we must solve a number of complex technical problems, relating to chemistry and to hydrogen technology, or at least in the next few years get this process going.

The first problem is due to the fact that hydrogen is currently too expensive as a fuel and is produced in amounts that are too small to satisfy the demand for it in the new branches of the national economy, which include not only power generation, but also chemical technology and materials science applications mentioned earlier.

Furthermore, current production of hydrogen from natural gas is itself not ecologically clean and not only leads to the consumption of nonrenewable resources of this valuable raw material, but is also accompanied by the generation of a considerable amount of carbon dioxide as a by-product. In the USSR alone, the emission of carbon dioxide into the atmosphere caused by hydrogen production, is about 18–20 million tonnes annually.

In view of this, improvement of the existing processes for electrochemical production of hydrogen by the electrolysis of water and water vapour is acquiring paramount importance along with the reduction in the associated energy consumption which may be achieved through the use of radically new materials and nonconventional chemical processes, primarily those based on renewable energy sources, such as solar energy, wind power, geothermal and hydrothermal processes, etc.

In the late 1970's a concept was promoted which is currently acquiring practical importance, namely that not only water and

water vapour can be used as raw materials for the production of hydrogen, but also hydrogen sulphide, at first glance an exotic chemical compound. Its natural resources are very large and may in principle serve as the basis for the development of industrial technologies. A solution to this scientific and technological problem would increase the availability of raw materials for hydrogen energy systems and hydrogen technology. In actual fact, the above concept has more general ecological and economical character, since in the first place it involves purification of natural hydrocarbon raw materials from highly toxic hydrogen sulphide and the use of the latter in the production of hydrogen and such a valuable chemical product as free sulphur.

Another problem with hydrogen energy systems is that, even with abundant cheap fuels or energy carriers, any branch of power generation (including that based on hydrogen) will flourish only if facilities are available for the effective use of chemical energy contained in the fuel and its conversion into electrical energy, thermal energy, etc.

For hydrogen, considering its unique physicochemical properties, such as calorific value which exceeds that of organic fuels by a factor of 3.5 and its low activation energy barrier with respect to catalytic oxidation, one can regard electrochemical power generators, which have 2–2.5 times greater efficiency than heat engines, as such facilities.

However, as opposed to heat engines which can in principle run on 'dirty' commercial hydrogen containing carbon oxides, water vapour, hydrocarbons and other impurities, electrochemical power generators are "capricious" and can use only high-purity hydrogen with no contaminants, which cause poisoning of catalytic contacts and reduce the efficiency of electrochemical oxidation. The above-mentioned high-technology branches both of chemical industry and of materials science place equally stringent requirements upon the purity of hydrogen.

Therefore, industrial hydrogen technology that would be appropriate for hydrogen energy systems would consist not only of ecologically clean technology for hydrogen production, based on the renewable sources of initial materials and energy, but would also involve a technology for the separation of industrial gas mixtures containing hydrogen and a high degree of purification of the latter that would reduce the content of impurities to $10^{-3}-10^{-4}$ vol.%.

At present, the most effective procedure for the production of high-purity hydrogen from industrial gases involves their preliminary separation and enrichment with hydrogen as the main component followed by the use of membrane technology, with palladium alloys acting as the materials for the selective filtration of hydrogen.

As long as the use of high-purity hydrogen is confined to certain special branches of metallurgy and the production of materials for the microelectronics and pharmaceutical industries, and does not exceed several thousand tonnes annually, this need may well be met on the basis of the existing technology. However, the situation will drastically change when hydrogen will be looked at as a basis for the creation of ecologically clean power systems for the 21st century. In this case the required annual production of low-cost high-purity hydrogen will amount to hundreds of thousands rather than thousands of tonnes. This task cannot be fulfilled with filters, using palladium alloys, simply because the required amount of palladium is not and will never be available. Alternative materials are required, which would act in a way similar to palladium alloys but would essentially differ in cost and suitability for mass production and consumption.

The second of the above problems is formulated in much the same manner, i.e. the creation of catalysts for the oxidation of hydrogen in electrochemical power generators. Materials containing platinum and platinum group metals serve as catalysts in contemporary fuel cells which are widely used in space and other special applications†. The consumption of platinum for each fuel cell with an output of 1 kW is about 100–200 mg. Even if this amount were to come down by a factor of 100 through improvements in the technology of production of electrode materials, the consumption of platinum metals required to furnish a fleet of, say, 50 million vehicles with an average power of 100–150 kW, woud nevertheless amount to approximately 500–600 tonnes, which is substantially more than the world annual extraction of platinum (not counting the USSR) of about 80 tonnes. Therefore, the creation of an ecologically clean electric car is in principle highly improbable, unless platinum-free catalysts for 'cold' electrochemical oxidation of hydrogen which would be competitive or at least comparable to platinum-based ones, are produced.

Fundamental studies on the chemistry of the interaction of hydrogen with metals and intermetallic compounds, conducted in the USSR and abroad[1–5] since 1968, offer real prospects for a successful search for and creation of catalysts that could replace palladium and the metals of the platinum family.

The "hydride dispersion" technology, which emerged in 1980–1982 on the basis of the above studies, allows dispersed metallic powders to be produced that are functionally similar to palladium and platinum group metals.

This technology is based on the ability of a large group of alloys of rare-earth elements, titanium, zirconium calcium, and magnesium, with transition metals which possess appropriate crystalline and electronic structures to reversibly absorb up to 1000–1200 times their volume of hydrogen, with a relatively small thermal effect (~5000 kcal per 1 kg of H_2). This process is accompanied by spontaneous comminution and formation of fine powders without resource to any mechanical processing. The resulting powders are characterised by a narrow particle size distribution, which depends on the number of sorption–desorption cycles, and "sterile" unoxidised surfaces. The sorption of hydrogen is also accompanied by a 15–25% increase in the volume of the metallic phase, its structure remaining unaltered and having a very low activation energy barrier. It is remarkable that the density of hydrogen nuclei in the hydride phase exceeds that of liquid hydrogen by a factor of 1.5–2.0.

A sponge which can be used an unlimited number of times for soaking up and squeezing out a liquid may serve as a model for these alloys. In our case hydrogen takes the place of the liquid, being sorbed on cooling and released on heating. Technological potentialities of these alloys are very high, being in the range of 10–15 thousand cycles.

It is important that hydrogen can also be sorbed from gas mixtures that contain as much as 80–90% of nitrogen, methane, inert gases, water vapour, oxygen, and carbon dioxide.

Another interesting feature of this process is its high selectivity, i.e. only hydrogen is sorbed. Therefore, the purity of hydrogen desorbed during the thermal decomposition of the hydride phase, i.e. on 'squeezing out the sponge', is very high, in excess of 99.999%.

† We are referring here to 'low-temperature' fuel cells. In the USSR, the USA and a number of other countries, strenuous efforts are currently under way to create prototypes of industrial 'high-temperature' fuel cells based on ceramic oxide materials.

Table 1 also shows various areas of application of metallic powders produced by the hydride dispersion technique. One should take special note of two processes, directly related to the ecological aspects of hydrogen technology and power engineering.

Table 1. Applications of dispersed metallic powders produced by the chemical dispersion technique. The powders are characterised by "sterile" unoxidised surfaces; absence of cold hardening and mechanical contamination; and narrow particle size distribution, controllable over a required range.

1.	Absorbents of hydrogen from industrial gas mixtures.
2.	Components of platinum-free catalysts for the oxidation of hydrogen in electrochemical fuel cells.
3.	Reversible sources of high-purity hydrogen, containing up to 1200 volumes of hydrogen per unit volume of a solid phase.
4.	Magnetic materials produced by compacting dispersed powders with the composition RCO_5, R_2CO_{17}, where R = Fe, B, etc.
5.	"Working media" in thermalsorption equipment and mechanisms.
6.	Components of mateirals with a high density of hydrogen nuclei.
7.	Highly efficient catalysts for processes involving activation of molecular hydrogen.

Problems involved in producing high-purity hydrogen, including its extraction from gas mixtures with low hydrogen content, may be resolved through the creation of absorption units, wherein a mass of a dispersed powder, or compacted material produced from it, kept together by an organic or metallic binder, performs sequentially in a sorption–desorption mode. The gas mixtures may be quite poor in hydrogen, containing as little as 10–15 vol.%.

The viability analysis of the sorption method carried out independently by several organisations, showed its high efficiency: the cost of obtaining 1 tonne of high-purity hydrogen from industrial hydrogen-bearing gases was found to be 1000–1500 roubles, which is approximately 2–3 times less than the current price.

A more promising, although technologically more complicated technique, involves the use of filters produced from dispersed powders containing rare-earth metals and metals of the iron group, these powders having been obtained by the hydride dispersion method. Judging from preliminary data (referring to 1988), such materials may well compete with palladium–silver alloys.

The second task is to create new catalysts for the oxidation of hydrogen, based on dispersed powders containing nickel, manganese, zirconium, etc. Studies along these lines are being conducted in the Soviet Union—the Electrochemistry Institute of the USSR Academy of Sciences, the Moscow State University and other organisations—and abroad, and are particularly actively pursued in Japan, USA, and EEC countries. Considerable progress has already been made in this direction. Current densities in electrodes, manufactured from compressed powders are now as high as 200–300 mA cm^{-2}, comparable to those in contemporary small fuel cells in which platinum-containing catalytic contacts are used.

Abroad, the hydride dispersion technique forms the basis for one of the fastest developing high-technology branches of industry.

In the USA, Japan, and EEC countries the envisaged annual production of hydrogen-absorbing alloys is about 1000 tonnes. Production of such alloys is apparently carried on an industrial scale in China, where hydride technology is being actively applied in the electronic industry, in the chemical industry, and for the production of high-quality magnetic materials. The world market prices for dispersed powders capable of reversibly absorbing hydrogen are currently about 400–500 US dollars per kg. Japanese experts estimate that by the year 2000 the internal market alone for the materials and articles involving the use of hydride technology will reach about 500 million US dollars.

Let us take a brief look at the model of the interaction of hydrogen with alloys of rare-earth metals, titanium, zirconium, and magnesium with transition metals (iron, cobalt, nickel, copper, chromium and vanadium) which is used as the basis for predicting the nature of such interaction in relation to the crystalline structure, chemical composition, and thermodynamic properties of the alloys.[6–8]

If an alloy capable of absorbing hydrogen is regarded as a 'sponge', reversible sorption of hydrogen should be possible under the following conditions:

1. The energy of activation of chemisorption of hydrogen at active centres on the surface of the metallic phase should be small. This surface can be modified by introducing into the alloy small admixtures of other metals so as to influence the physicochemical properties of the hydride phase in the desired direction.

2. The structure of the alloy should have a crystal-chemical 'predisposition' to the sorption of hydrogen, this predisposition being characterised by the presence of cavities or voids of definite size and configuration.

3. For virtually all alloys that are potential hydrogen sorbents, a reaction alternative to the sorption of hydrogen is thermodynamically possible, for example, a chemical reaction of destruction yielding binary hydrides and free transition metals which do not absorb hydrogen. The probability or possibility of a reaction of this kind at a certain temperature and hydrogen pressure is predictable, given the main thermodynamic properties of the initial alloy. On this basis chemists may design and produce any alloy whose sorption parameters would be optimised to meet specific technical conditions required by chemical engineers and designs of equipment for various purposes.

This allows us to be optimistic about prospects of using the hydride technology for creating in the near future ecologically clean power engineering complexes, based on a wide use of hydrogen as the chemical raw material, energy carrier, and medium for conducting technological operations in sterile conditions.

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Brief communications

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Prospects and current problems in the reduction of emission from automobile transport

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The contribution to atmospheric pollution by automobile transport, which amounts to 15–25% relative to the overall pollution, increases to 75–80% (with respect to CO) when pollution in cities is considered.

Real tests have shown that the limiting permissible concentrations have been exceeded by a factor of 7–16 with respect to components for which norms have been laid down in relation to automobile transport, the factor increasing to 20–50 with respect to the overall emissions subject to norms let alone the presence of indirectly normalised and non-normalised components (lead and sulphur compounds, aldehydes, etc.) as well as the "background" (inadequate purification of water, contamination of food products). A similar situation is characteristic of at least 116 cities in the USSR. The possible measures for the planned reduction of emissions from transport, in Moscow for example, could actually prove ineffective because of the growth of the transport fleet and its long renewal cycle (up to 20 years).

The USSR tends to adopt the normalisation level established by the EEC and UNO rules, although the majority of the European countries are going over to the stricter U.S. norms. However, even the EEC and UNO norms presupposes the use of only non-ethylated (unleaded) petrol as the fuel and hence the catalytic purification of spent gases. In our country, the presence of norms for automobiles with catalytic converters (production for export with imported converters) is combined with "milder" norms for automobiles without converters (for internal use). Such "dual" normalisation reflects the situation in which there is a lack of material means for the fulfilment of stricter norms. Thus acording to EEC estimates, the changeover by 1991 to non-ethylated fuels will require 2.7–3.5 billion dollars in capital investment. One must recognise that, as a result, there has been no reduction in automobile transport emission in our cities. Therefore in the general prospective programme for the reduction of emissions from means of transportation, it is essential to concentrate on the rapid improvement of the ecological situation in cities.

The problem of developing promising means of transportation with improved economic parameters includes the search for ecologically acceptable energy carriers. The most promising of these (hydrogen) cannot be regarded as an "ecologically clean" fuel because of the formation, on its combustion in air, of NO and the thermal pollution common to all energy consuming devices. A real effect can be achieved even at the present time by using liquified and compressed gaseous fuels.

The use of gaseous fuels in engines with a homogeneous mixture makes it possible to go over to the combustion of leaner mixtures, taking into account the effect of the diffusional enrichment of the flame front in the lighter component. In diesel engines, the use of gaseous fuel involves the solution of the problem of the reliable ignition of the gaseous fuel stream.

The most effective and realistic procedure is the employment of soot filters in diesel engines and of controlled catalytic converters in petrol engines. However, such converters require an oxygen sensor, an electronic system for the control of fuel injection, and the use of a fuel without a lead antiknock agent. The same measures can be taken in the solution of urgent ecological problems in cities, including Moscow. Here one can assume that purely technical problems are not of decisive importance. In the first place, it is essential to solve the following main problems:

The specification of norms for harmful emissions by legal organs with an expert assessment by an independent competent organisation (the USSR Academy of Sciences) instead of normalisation by what is in fact a government department.

The establishment of the magnitude of fines on the grounds that it is preferable to finance nature-protecting measures rather than pay for the pollution of the atmosphere under conditions where industrial undertakings are economically truly independent.

Transition from financing the research programmes set up by the researchers themselves to the creation of a scientific-industrial association with target financing and the rights of the director (or general constructor) concerning its utilisation.

A combined approach to decreasing the contamination of a city with gases, the reconstruction of the network of highways, and the development of green zones and plantations (including for this purpose financial means received from the increased expenditure on transport).

Thus the current task of reducing sharply the level of contamination of cities by gases is organisational rather than technical in character, which should be taken into account in the development of an ecological programme.